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VISCOSITY AND FLUIDITY.[1]

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PART I.

Liquid Mixtures.

In the course of some work carried out in the chemical laboratory of the Johns Hopkins University and published under the title "The Conductivity and Viscosity of Solutions of Certain Salts in Mixtures of Acetone with Methyl Alcohol, Ethyl Alcohol and Water,"[2] it was observed that solutions of potassium iodide, in mixtures of acetone with methyl alcohol or ethyl alcohol, gave conductivities which were proportional to the amounts of the components of the mixture. In other words, when the conductivity curves were plotted they were found to be straight lines to within the limits of experimental error. When the fluidities of these solutions were found and plotted, similar results were obtained. It seemed possible, therefore, to explain the above changes in conductivity as due simply to changes in the fluidity of the solutions.

[1] The author is indebted to Prof. Joseph Ames and to Dr. H. Bradshaw for valuable suggestions and corrections.

[2] Jones and Bingham: THIS JOURNAL, 34, 481 (1905).

The viscosity curves for the above mixtures are sagged, *i. e.*, the viscosities of the mixtures are not directly proportional to the amounts of the components. Thus it seemed necessary to consider whether fluidities or viscosities are directly comparable with conductivities.

For this purpose it may be supposed that a mixture is made of two liquids which are composed of particles that have no unusual action upon each other, *i. e.*, do not form new aggregations of any kind. Two monomolecular liquids, which do not form complexes on mixing, would fulfil this condition. Further, it may be assumed that this mixture is allowed to flow through a tube. The more rapidly moving particles would be held back by those moving more slowly and the resulting motion would appear to be a mean value proportionate to the relative amounts of the components. In other words, the resulting fluidity would be the sum of the partial fluidities of the components. It should be noticed that this simple relation cannot be reasonably assumed when we consider viscosities instead of fluidities. Formulated, the above relation is

$$(m_1 + m_2)\Phi = m_1\phi_1 + m_2\phi_2 \ldots\ldots\ldots (1),$$

where m_1 and m_2 are the amounts of the components, ϕ_1 and ϕ_2 their respective fluidities and Φ the resultant fluidity.

This is similar to the conception which we have in electricity, where the conductance of two or more conductors, in parallel, is represented by the sum of their separate conductances. The conductance of a pair of conductors, of different material, is, for a unit length,

$$(\sigma_1 + \sigma_2)C = c_1\sigma_1 + c_2\sigma_2,$$

where σ_1 and σ_2 are the areas of cross-section of the conductors, c_1 and c_2 their respective conductances, and C the resulting conductance.

If this reasoning is correct, conductivity and fluidity are strictly comparable.

It was stated above that it cannot be reasonably assumed that viscosities are additive. It is evident at once that, if fluidities are additive, viscosities cannot be additive. By

making m_1 and m_2 the amounts of the two components of a binary mixture, expressed in percentages, equation (1) becomes,

$$\Phi = m_1\phi_1 + (1 - m_1)\phi_2 \quad \ldots\ldots\ldots\ldots (2),$$
$$= m_1(\phi_1 - \phi_2) + \phi_2.$$

If η_1 and η_2 represent the viscosities of the components and H that of the mixture, then, since viscosity is the reciprocal of fluidity, we have from (2),

$$\frac{1}{H} = \frac{m_1}{\eta_1} + \frac{1 - m_1}{\eta_2}$$
$$\eta_1\eta_2 = [m_1\eta_2 + (1 - m_1)\eta_1]H$$
$$= [m_1(\eta_2 - \eta_1) + \eta_1]H.$$

If we let

$$m_1(\eta_2 - \eta_1) + \eta_1 = m'_1(\eta_2 - \eta_1)$$

we have

$$m'_1 H = \frac{\eta_1\eta_2}{\eta_2 - \eta_1} \quad \ldots\ldots\ldots\ldots (3).$$

Since $\frac{\eta_1\eta_2}{\eta_2 - \eta_1}$ is a constant, equation (3) represents an equilateral hyperbola whose Y-axis is a distance $\frac{\eta_1}{\eta_2 - \eta_1}$ to the left of the origin to which equation (1) is referred. Thus we reach the conclusion that the hyperbola is the normal curve for the viscosities of simple mixtures.

Before this conclusion can be accepted as final, it will, of course, be necessary to show that, in a large number of cases, the fluidity curves of mixtures do in fact approximate to straight lines.

In the case of divergence from the straight line, it would be expected that new factors would be found entering to change the conditions. Such tendencies should manifest themselves in physical properties other than fluidity alone. It should be noted that, thus far, nobody has been able to establish any certain relations in mixtures between *viscosity* and other phys-

ical properties. The deviations in viscosity are quite uniformly greater than would be expected.

It has already been shown[1] that, in the particular case of water and acetone, there is a large deviation of the fluidity curve from a straight line. There is also a large contraction and evolution of heat on mixing. These phenomena seem to be general in the case of mixtures of water with other liquids. Traube[2] and others have studied a large number of such cases. In every instance there is a very great decrease in fluidity from what we should expect according to the rule of averages.

Unfortunately, there are no data relating to the other physical properties of these mixtures, hence it is impossible to use, in this connection, the data available. There exist, however, considerable data regarding the viscosity of non-aqueous mixtures. From these I have calculated the fluidities given in this paper. References to the sources of the material have been made in connection with the tables. Other data than those given have been considered, but, since no new relations were brought out, they have not been included here.

In Fig. I. and in Tables I. to VIII. are represented the fluidities of several pairs of liquids whose viscosity curves are only very slightly sagged. Ethyl acetate and carbon bisulphide, I., toluene and carbon bisulphide, II., toluene and ethyl acetate, III., form a trio of pairs of substances whose viscosity curves are very slightly sagged. On plotting the fluidities the curves closely approximate straight lines.

Benzene and toluene, IV., and benzene and chloroform, V., have viscosity curves which are almost identical and are nearly a straight line. The fluidities also give us a straight line, to the limits of experimental error. Since it is not practicable to draw two curves for the two pairs of substances, the points for the benzene and chloroform mixtures are indicated by crosses in the figure.

Benzene and chloroform, V, carbon tetrachloride and chloroform, VI., and carbon tetrachloride and benzene, VII., form a second trio of pairs whose fluidities are again very nearly proportional to the concentration of the components.

[1] Jones and Bingham: THIS JOURNAL, 34, 540 (1905). Figs. XXI. and XXII.
[2] Ber. d. chem. Ges., 19, 871 (1886).

The above values have been taken from Linebarger.[1] Thorpe and Rodger,[2] commenting on his data, made the interesting observation that the viscosity curves approach straight lines when the viscosities of the components are not very different. In their own words, "As a rule, the greater the difference between the viscosities of the pure liquids, the greater is the difference between the calculated and the observed values of the mixtures." From the new point of view, the reason for this is immediately apparent. When η_1 and η_2 of equation (3) are nearly equal, the value of $\eta_2 - \eta_1$ is very small and the distance $\frac{\eta_1}{\eta_2 - \eta_1}$ becomes correspondingly great. The portion of the hyperbola, of which the observed viscosity curve forms a part, is, therefore, at a considerable distance from the vertex of the hyperbola, hence the curvature is small. We may get an idea of this distance from the figure by imagining the fluidity curves prolonged until they cross the X-axis. The point of intersection in each case will be the origin for the equilateral hyperbola of equation (3).

Table I.[3]*—Fluidity of Mixtures of Ethyl Acetate and Carbon Bisulphide at 25°.*

Percentage of carbon bisulphide.	Viscosity.	Fluidity.
0.000	0.00462	216.5
33.587	0.00416	240.4
60.754	0.00389	257.1
83.641	0.00367	272.5
100.000	0.00358	279.3

Table II.[1]*—Fluidity of Mixtures of Toluene and Carbon Bisulphide at 25°.*

Percentage of carbon bisulphide.	Viscosity.	Fluidity.
0.000	0.00541	184.8
36.758	0.00469	213.2
62.008	0.00417	239.8
92.731	0.00370	270.3
100.000	0.00358	279.3

[1] Am. J. Sci., 2, 331 (1896).
[2] J. Chem. Soc., 71, 361 (1897).
[3] Linebarger: Am. J. Sci., 2, 331 (1896).

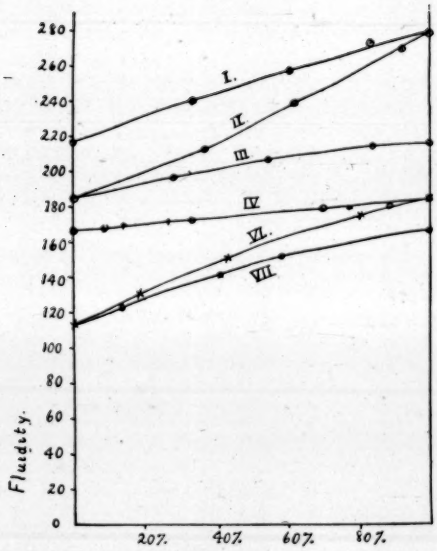


Figure 1.

I. = Ethyl acetate and carbon bisulphide.
II. = Toluene and carbon bisulphide.
III. = Toluene and ethyl acetate.
IV. = Benzene and toluene.
V. = Benzene and chloroform.
VI. = Carbon tetrachloride and chloroform.
VII. = Carbon tetrachloride and benzene.

Table III.[1]*—Fluidity of Mixtures of Toluene and Ethyl Acetate at 25°.*

Percentage of ethyl acetate.	Viscosity.	Fluidity.
0.000	0.00539	185.5
28.745	0.00509	196.5
54.699	0.00481	207.9
84.292	0.00466	214.6
100.000	0.00462	216.5

[1] Linebarger: Am. J. Sci., 3, 331 (1896).

Table IV.[1]*—Fluidity of Mixtures of Benzene and Toluene at 25°.*

Percentage of toluene.	Viscosity.	Fluidity.
0.000	0.00599	166.9
8.444	0.00594	168.4
33.424	0.00579	172.7
69.412	0.00558	179.2
89.009	0.00555	180.2
100.000	0.00541	184.8

Table V.[1]*—Fluidity of Mixtures of Benzene and Chloroform at 25°.*

Percentage of chloroform.	Viscosity.	Fluidity.
0.000	0.00599	166.9
14.169	0.00587	170.4
27.220	0.00581	172.1
76.990	0.00557	179.5
93.033	0.00546	183.2
100.000	0.00540	185.2

Table VI.[1]*—Fluidity of Mixtures of Carbon Tetrachloride and Chloroform at 25°.*

Percentage of chloroform.	Viscosity.	Fluidity.
0.000	0.00883	113.25
18.828	0.00761	131.41
42.723	0.00659	151.75
80.731	0.00569	175.7
100.000	0.00540	185.2

Table VII.[1]*—Fluidity of Mixtures of Carbon Tetrachloride and Benzene at 25°.*

Percentage of benzene.	Viscosity.	Fluidity.
0.000	0.00883	113.25
13.727	0.00808	123 76
40.780	0.00706	141.64
58.600	0.00660	151.52
100.000	0.00599	166.9

In Fig. 2 and in Tables VIII. to XIV. are represented the fluidities of several pairs of substances whose viscosity curves are considerably sagged. Figures showing the character of these viscosity curves have been published by Dunstan.[2] Ben-

[1] Linebarger: Am. J. Sci., **2**, 331 (1896).
[2] J. Chem. Soc., **85**, 821 (1904).

zene and ethyl acetate, VIII., nitrobenzene and ethyl acetate, IX., and nitrobenzene and benzene, X., form a third trio of pairs of substances. The second gives a curve that is somewhat sagged. The others are nearly straight. Ethyl alcohol and acetone, XI., give a straight line to the limits of experimental error. I have observed, moreover, that there is no perceptible contraction or evolution of heat on mixing these components. Turpentin and toluene, XII., and ethyl benzoate and toluene, XIII., give figures that are slightly curved but in opposite directions. In this connection it should be recalled that in certain cases there is a very marked change which takes place when two liquids are mixed, similar to that which is observed in all of the aqueous mixtures. Hence it would not be surprising if *no* two liquids give a curve that is absolutely a straight line; but when there are deviations in fluidity from the normal, there ought also to be evidence of abnormality in other physical properties. Since no such evidence is available in the above cases, we must be satisfied that the curves are approximately straight lines in such a large number of instances.

It will be helpful, at this point, to give some of the conclusions of previous workers on the viscosity observations, because considerations of fluidity throw some light upon those points that seemed quite obscure when viscosities alone were considered. Dunstan,[1] for example, remarks that "The law of mixtures is never accurately obeyed and divergences from it seem to be more clearly marked out in the case of viscosity than with other properties, such as refractive index." Thorpe and Rodger[2] say: "The observations described in this paper afford additional evidence of the fact indicated by Wijkander[3] and supported by Linebarger,[4] that the viscosity of a mixture of miscible and chemically indifferent liquids is rarely, if ever, under all conditions, a linear function of the composition. It seldom happens that the liquid in a mixture preserves the particular viscosity it possesses in the unmixed condition. To

[1] J. Chem. Soc., **85**, 819 (1904).
[2] *Ibid.*, **71**, 374 (1897).
[3] Lunds. Phys. Sallsk. Jubelschrift, 1878. Weid. Beibl., **8**, 3 (1879).
[4] Am. J. Sci., **11**, 331 (1896).

judge from the instances heretofore studied, the viscosity of the mixture is, as a rule, uniformly lower than the mixture law would indicate, but no simple relation can yet be traced between the viscosity of a mixture and that of its constituents." They are so confident that there is some uncomprehended principle which causes the viscosity curve to always fall below the straight line, that they make the following statement[1] in regard to the viscosity curves of Linebarger, which *are* very nearly straight lines: "The observed viscosities in general are less than those calculated by the mixture rule, except, possibly, in the case of mixtures of benzene and chloroform and mixtures of carbon disulphide with benzene, toluene, ether and acetic ether, where, possibly, the temperature of observation (25°) was too near the boiling-point of the carbon disulphide to make any specific influence, which that liquid might exert at lower temperatures, perceptible." This assumption is not necessary according to the new view. Thus are explained not only the deviations from the values of the viscosities expected according to the rule of mixtures, but also even those perplexing cases where the rule is obeyed.

Table VIII.[2]*—Fluidity of Mixtures of Benzene and Ethyl Acetate at 25°.*

Percentage of ethyl acetate.	Viscosity.	Fluidity.
0.000	0.00599	166.9
19.197	0.00551	181.5
48.596	0.00487	205.3
84.406	0.00442	226.2
100.000	0.00434	230.4

Table IX.[2]*—Fluidity of Mixtures of Nitrobenzene and Ethyl Acetate at 25°.*

Percentage of ethyl acetate.	Viscosity.	Fluidity.
0.00	0.01834	54.52
24.47	0.01204	83.05
43.90	0.00889	112.49
77.10	0.00582	171.8
100.00	0.00434	229.9

[1] J. Chem. Soc., 71, 361 (1897).
[2] Linebarger: Am. J. Sci., 3, 331 (1896).

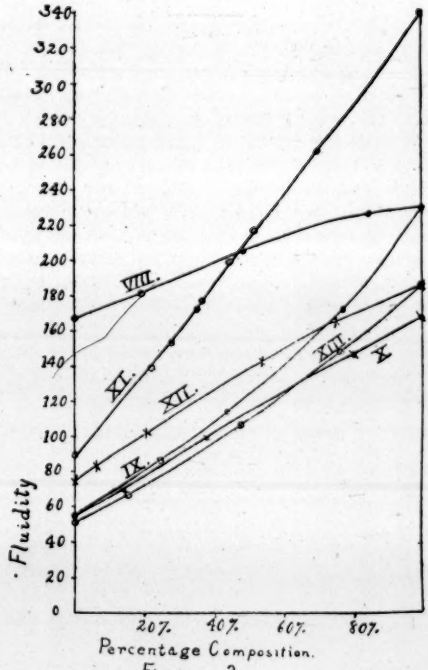


Figure 2.

VIII. = Benzene and ethyl acetate.
IX. = Nitrobenzene and ethyl acetate.
X. = Nitrobenzene and benzene.
XI. = Ethyl alcohol and acetone.
XII. = Turpentin and toluene.
XIII. = Ethyl benzoate and toluene.

Table X.[1]*—Fluidity of Mixtures of Nitrobenzene and Benzene at 25°.*

Percentage of benzene.	Viscosity.	Fluidity.
0.000	0.01834	54.53
14.394	0.01417	69.58
37.610	0.01017	98.33
80.053	0.00681	146.8
100.000	0.00599	166.9

Table XI.[1]*—Fluidity of Mixtures of Ethyl Alcohol and Acetone at 25°.*

Percentage of acetone.	Viscosity.	Fluidity.
0.00	0.01115	89.71
22.46	0.007168	139.50
27.77	0.006510	153.61
35.11	0.005797	172.3
36.83	0.005636	177.3
43.38	0.005162	193.7
44.50	0.005028	198.9
51.57	0.004620	216.5
70.34	0.003836	260.7
100.00	0.003125	320.0

Table XII.[2]*—Fluidity of Mixtures of Turpentin and Toluene at 25°.*

Percentage of toluene.	Viscosity.	Fluidity.
0.000	0.01343	74.47
6.791	0.01192	83.88
20.654	0.00978	102.2
53.701	0.00701	142.6
75.091	0.00607	164.7
100.000	0.00539	185.5

Table XIII.[2]*—Fluidity of Mixtures of Ethyl Benzoate and Toluene at 25°.*

Percentage of toluene.	Viscosity.	Fluidity.
0.000	0.01954	51.18
15.282	0.01495	66.89
47.322	0.00939	106.5
76.170	0.00679	147.3
100.000	0.00539	185.5

[1] Dunstan: J. Chem. Soc., 85, 822 (1904).
[2] Linebarger: Am. J. Sci., 2, 331 (1896).

In Fig. 3, Tables XIV. to XVII., are represented another trio of pairs of substances—carbon bisulphide and ether, XIV., benzene and ether, XV., and benzene and carbon bisulphide, XVI. The curves for the first two are very nearly straight lines, that for the third is slightly sagged.

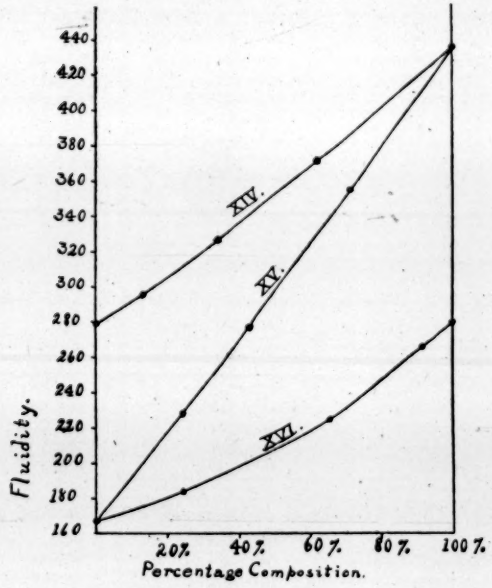


Figure 3.

XIV. = Carbon bisulphide and ether.
XV. = Benzene and ether.
XVI. = Benzene and carbon bisulphide.

Table XIV.[1]*—Fluidities of Mixtures of Carbon Bisulphide and Ether at 25°.*

Percentage of ether.	Viscosity.	Fluidity.
0.000	0.00358	279.3
13.100	0.00338	295.9
34.367	0.00306	326.8
62 759	0 00269	371.7
100.000	0.00230	434.8

Table XV.[1]*—Fluidity of Mixtures of Benzene and Ether at 25°.*

Percentage of ether.	Viscosity.	Fluidity.
0.000	0.00599	166.9
24.309	0 00438	228.3
43 076	0.00362	276 2
71.424	0.00282	354.6
100.000	0.00230	434.8

Table XVI.[1]*—Fluidity of Mixtures of Benzene and Carbon Bisulphide at 25°.*

Percentage of carbon bisulphide.	Viscosity.	Fluidity.
0 000	0.00599	166.9
24 114	0.00544	183 8
65 142	0.00446	224.2
91.127	0.00376	266.0
100.000	0.00358	279.3

Fig. 4, Tables XVII. and XVIII., represent the fluidities of mixtures of methyl iodide and carbon bisulphide at 0°, 20° and 40°, and of carbon tetrachloride and benzene at 0°, 30° and 60°. The fluidity values for methyl iodide and carbon bisulphide mixtures are slightly greater than normally would be expected; but at low temperatures the effect is less marked. Now this increase in the fluidity may be explained as due to some change taking place when the components are brought together—perhaps a breaking down of a few molecular aggregations, which would naturally be facilitated by heat. This view accords with the facts and, fortunately, Thorpe and Rodger[2] furnish other data that support it. They found that when methyl iodide and carbon bisulphide are mixed an *expansion* occurs which is quite marked. With carbon tetra-

[1] Lineharger: Am. J. Sci., 3, 331 (1896).
[2] J. Chem. Soc., 71, 367 (1897).

chloride and benzene there is also an elevation of the fluidity curves above the normal, but it is much less pronounced than in the previous case, especially at low temperatures. Thorpe and Rodger found that when carbon tetrachloride and benzene are mixed there is no expansion at all, but perhaps a very slight contraction.

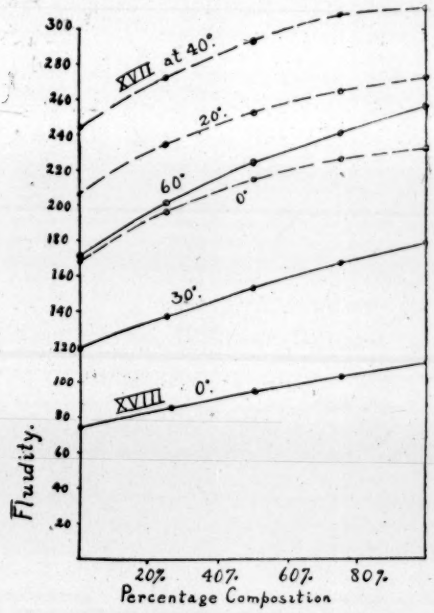


Figure 4.

XVII. = Methyl iodide and carbon bisulphide at 0°, 20° and 40°.
XVIII. = Carbon tetrachloride and benzene at 0°, 30° and 60°.

Table XVII.[1]*—Fluidity of Mixtures of Methyl Iodide and Carbon Bisulphide at 0°, 20° and 40°.*

Percentage of carbon bisulphide.	Fluidity at 0°.	Fluidity at 20°.	Fluidity at 40°.
0	168.1	206.6	244.5
25	196.5	234.2	272.1
50	214.6	252.5	293.3
75	226.2	265.3	307.7
100	232.6	273.2	312.5

Table XVIII.[1]*—Fluidity of Mixtures of Carbon Tetrachloride and Benzene at 0°, 30° and 60°.*

Percentage of benzene.	Fluidity at 0°.	Fluidity at 30°.	Fluidity at 60°.
0	74.41	119.05	171.8
25	84.75	137.93	201.6
50	94.34	153.14	224.7
75	103.09	167.8	241.5
100	110.62	178.6	256.4

Fig. 5 represents the fluidities of chloroform and ether at 0° and 30°. In this case there is a pronounced sagging in the fluidity curve. The effect is less marked at the higher temperature. If the view which I suggest is correct, it must be assumed that when the chloroform and ether are mixed, a change takes place, which causes the fluidity to be abnormal. It is convenient to conceive of this as a tendency on the part of these liquids to form molecular aggregations with each other. Were these formed, they would be less stable at the higher temperatures and, consequently, the sagging would be less pronounced. This again accords with the facts, but Thorpe and Rodger[1] have furnished other data that are of interest. When chloroform and ether are mixed there is "a considerable evolution of heat and a notable contraction." They have measured this contraction at 0° for the four mixtures with which they worked. They found that the greatest contraction took place in the mixture containing 40.14 per cent of ether and 59.86 per cent of chloroform. On plotting the fluidities on a large scale and measuring the deviation

[1] Thorpe and Rodger: J. Chem. Soc., 71, 370, 366 (1897).

from the normal fluidity curve the maximum deviation is found to be most probably in a mixture containing 39 per cent of ether; but on account of the large degree of curvature and the scarcity of the determined points, it is impossible to locate the exact position of greatest deviation within some 3° of this value. On plotting the contractions in volume as ordinates and the percentage compositions as abscissae, the maximum contraction is seen to be most probably in a mixture containing less than 40 per cent of ether and perhaps less than 39 per cent. Here again, however, it is impossible to locate the exact point. Thus in the only case where the data are sufficient, there is a quantitative agreement between the abnormality in fluidity and volume.

It should be mentioned that the viscosity curves for this pair of substances show an inflection-point. To explain this according to the view that viscosities are additive, it was necessary to make two very doubtful assumptions.[1] According to the view here presented, only one new assumption is necessary, *viz.*, that there is a change which takes place when these components are mixed. This assumption has been shown to be entirely supported by the facts.

Chloroform and ether thus present a case exactly similar to what is found quite uniformly in aqueous mixtures, there being contraction, evolution of heat and a large decrease in fluidity, but in a less pronounced degree.

It was convenient to refer to this change as though due to molecular aggregations formed by the mutual action of the two liquids. In another connection the expression "breaking down of molecular aggregations" was employed. It is not intended by these phrases to introduce a theory as to the cause of the abnormality, the terms have been previously employed in viscosity discussions and are convenient as names for phenomena. It may be that the true explanation of the abnormality is more deep-seated, for if it is true that viscosity, in liquids, is dependent upon the attractions between the molecules, then, if, for any reason, there is a contraction on mixing two liquids, the molecules will be brought closer together than would

[1] J. Chem. Soc., 71, 374 (1897).

otherwise be expected and the attractions between the molecules will be increased. This will cause a decrease in the fluidity from the value calculated by the rule of mixtures. In a similar manner an expansion, on mixing the liquids, will cause an increase in the fluidity. Of course two liquids may form these molecular aggregates on mixing whenever there is a contraction, but there is no proof that the formation of such aggregates is necessary.

Ethyl alcohol and ethyl mercaptan, XX., give fluidities which are somewhat similar to those of chloroform and ether, but data in regard to other physical properties of these mixtures are not available.

Table XIX.[1]*—Fluidity of Mixtures of Chloroform and Ether at 0° and 30°.*

Percentage of ether.	Viscosity at 0°.	Fluidity at 0°.	Viscosity at 30°.	Fluidity at 30°.
0.00	0.00700	142.9	0.00511	195.7
15.94	0.00678	147.5	0.00472	211.9
40.14	0.00562	177.9	0.00382	261.8
59.80	0.00440	227.2	0.00310	322.6
79.30	0.00350	285.7	0.00254	393.7
100.00	0.00286	349.6	0.00212	471.7

Table XX.[2]*—Fluidity of Mixtures of Ethyl Alcohol and Mercaptan at 25°.*

Percentage of mercaptan.	Viscosity.	Fluidity.
0.00	0.01113	89.5
3.48	0.01048	95.4
9.47	0.009731	102.8
12.30	0.009305	107.5
13.88	0.008559	114.2
16.25	0.008385	119.3
32.54	0.006525	153.2
35.97	0.006119	163.4
44.76	0.005821	171.8
68.05	0.004083	244.9
100.00	0.002091	478.2

[1] Thorpe and Rodger: J. Chem. Soc., 71, 373 (1897).
[2] Dunstan: *Ibid.*, 85, 821 (1904).

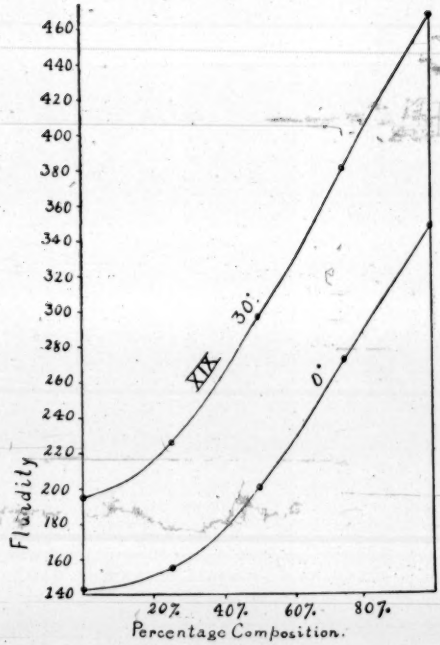


Figure 5.

XIX. = Chloroform and ether at 0° and 30°.

In Fig. 6 are shown three other examples of pairs of liquids which behave abnormally, but the data in regard to them is not sufficiently complete to furnish any new information. Ethyl alcohol and carbon bisulphide, XXI., give a considerably sagged curve; ethyl alcohol and benzene, XXII., show a sharp maximum in a 94 per cent mixture; benzaldehyde and ethyl alcohol, XXIII., also show a maximum in fluidity.

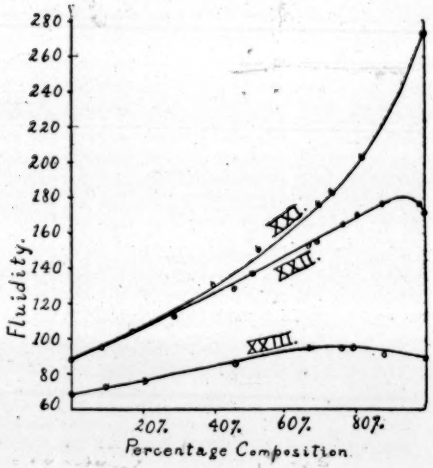


Figure 6.

XXI. = Ethyl alcohol and carbon bisulphide.
XXII. = Ethyl alcohol and benzene.
XXIII. = Benzaldehyde and ethyl alcohol.

Table XXI.[1]*—Fluidity of Mixtures of Ethyl Alcohol and Carbon Bisulphide at 25°.*

Percentage of carbon bisulphide.	Viscosity.	Fluidity.
0.00	0.01113	89.85
16.91	0.009448	105.84
19.29	0.009535	104.88
25.64	0.009065	110.32
32.31	0.008407	118.95
39.50	0.007621	131.21
52.82	0.006659	150.17
69.95	0.005669	176.35
73.50	0.005466	182.9
81.93	0.004926	203.1
100.00	0.003656	273.6

[1] Dunstan: J. Chem. Soc., **85**, 820 (1904).

Table XXII.[1]*—Fluidity of Mixtures of Ethyl Alcohol and Benzene at 25°.*

Percentage of benzene.	Viscosity.	Fluidity.
0.00	0.011130	88.50
8.47	0.01013	98.72
17.00	0.009545	104.77
28.90	0.008837	113.16
45.60	0.007758	128.89
50.91	0.007282	137.33
67.58	0.006514	153.52
69.49	0.006465	154.68
76.53	0.006071	164.71
80.38	0.005885	170.0
88.03	0.005669	176.2
98.86	0.005668	176.3
100.00	0.005821	171.8

Table XXIII.[1]*—Fluidity of Mixtures of Benzaldehyde and Ethyl Alcohol at 25°.*

Percentage of ethyl alcohol.	Viscosity.	Fluidity.
0.00	0.01445	69.20
9.37	0.01362	73.42
20.68	0.01308	76.48
46.04	0.01158	86.36
67.53	0.01041	96.06
76.40	0.01051	95.15
79.33	0.01050	95.24
88.35	0.01092	91.58
100.00	0.01113	89.86

Previous observers, studying the viscosity of mixtures, expected to find the viscosity to be normally a linear function of the composition, but the exceptions were so frequent that they were assumed to be the rule. Nevertheless, there were a few perplexing cases where the viscosity did obey the mixture-rule. In this paper I have tried to show, from theoretical considerations, that *fluidities alone* should be additive and that the normal viscosity curve should be hyperbolic. I have also taken recorded viscosity data and shown that, *in a large number of instances, the fluidity curves of mixtures are nearly straight lines*. The viscosity data for aqueous mixtures have not been

[1] Dunstan: J. Chem. Soc., 85, 822 (1904).

considered here because, when water is mixed with other liquids, there evidently occurs some unusual change, for there is, in general, a contraction, an evolution of heat and a large decrease in fluidity. In the case of chloroform and ether a somewhat similar condition is observed. Thorpe and Rodger[1] found a considerable evolution of heat and a notable contraction. I have shown that there is a considerable sagging in the fluidity curve, and that the maximum deviation occurs in the mixture where there is the greatest contraction. Methyl iodide and carbon bisulphide expand on mixing and I have found that there is an increase in the fluidity over the values expected by the mixture-rule. Thus there seems to be a parallelism between the changes in fluidity and the other physical properties for which data are available.

The departures of the viscosity curves from the straight line are, therefore, satisfactorily explained and those cases which follow the mixture-rule are equally well explained. The inflection-point in the viscosity curve of chloroform and ether is also now accounted for in a manner which is in harmony with the facts.

I hope, later, to compare the fluidities of aqueous mixtures with various other physical properties, and to investigate more closely the cases which seem to show abnormality.

I have done a good deal of work upon the fluidities of pure liquids at different temperatures, using the elaborate viscosity data of Thorpe and Rodger.[2] The results will be communicated in a second paper. The relations are more interesting than those which appear with liquid mixtures, because any tendency on the part of two liquids to form molecular aggregates with each other is eliminated; the conditions are simpler and, therefore, a maximum in such fluidity curves would not be expected.

The curves are very nearly straight lines for all unassociated compounds and the fluidities of the compounds, in a homologous series, at any given temperature, decrease regularly as the molecular weight increases. Thus, when the fluidities are

[1] J. Chem. Soc., **71**, 370 (1897).
[2] Phil. Trans., **185A**, 307 (1894).

plotted as ordinates and the temperatures as abscissae, a series of nearly straight and parallel lines, inclined at a definite angle to the X-axis, are obtained. With associated compounds abnormalities appear, as would be expected. The fluidities of compounds in a homologous series, notably the acids, no longer increase regularly as the molecular weight increases. This is especially noticeable among the first members of the series. With the heavy alcohols, at low temperatures, the fluidity increases more rapidly than would be anticipated, the fluidity curves becoming fairly straight only at very high temperatures. This is in harmony with the theory of Kohlrausch[1] and Bousfield and Lowry,[2] that the fluidity of a liquid, on simple cooling, should never become zero, but asymptotic to the X-axis. Since the fluidity curve, at high temperatures, becomes nearly a straight line inclined at a definite angle to the X-axis, there is reason for supposing that the complete formula for the fluidity of a pure liquid at different temperatures would be a hyperbola. The formula of viscosity commonly used, $\eta = \frac{C}{1 + \alpha t + \beta t^2}$, where C, α and β are constants, tacitly assumes, however, that the fluidity curve has a parabolic form, since

$$\frac{1}{\eta} = \phi = (1 + \alpha t + \beta t^2)/C.$$

This leads, therefore, to the same conclusion that Kohlrausch[3] reached by a different method, that this formula cannot express the viscosity relation over the widest possible range of temperature. An expression of the form

$$\phi = \frac{c}{\phi - at - b},$$

where c, a and b are constants would, apparently, be more suited to the theoretical requirements; it gives good results in certain cases that have been tested, when the values of the fluidities calculated are compared with those taken directly

[1] P. Roy. Soc., 71, 344 (1903).
[2] *Ibid.*, 70, 42 (1902).
[3] *Loc. cit.*

from the viscosity observations. It is hoped that further work along this line will give some light on the association or molecular aggregations in pure liquids, which cause the bending of the fluidity curves.

LEIPZIG, September, 1905.

REACTIONS BETWEEN LEAD CHLORIDE AND LEAD ACETATE IN ACETIC ACID AND WATER SOLUTIONS.

BY JOHN WHITE.

The chloride, bromide, iodide and sulphate of lead, and perhaps other salts as well, dissolve much more readily in water solutions of the alkali acetates and tartrates than in water alone. In the case of the sulphate, this fact has long been known and made use of for purposes of analysis. Since the reactions have been but slightly studied, some time ago I began an investigation of them, with the object of determining their character, if possible. One paper upon the subject has already been published;[1] it dealt with the reactions between lead iodide and the acetates. Since then the work has been interrupted, and it has only recently been possible to take it up again.

Meanwhile certain confirmatory evidence as to the existence of compounds of the type described in the previous paper has been furnished through the work of Colson[2] on barium acetochloride, and of Lemoult[3] on lead acetothiosulphate. In the present paper I shall endeavor to present additional evidence for the correctness of the formulas which have been suggested. No attempt has been made to formulate these compounds strictly in accordance with any of the existing theories of structure, because no definite information concerning their molecular complexity has, as yet, been obtained.

No very satisfactory explanation of the increased solubility of

[1] THIS JOURNAL, 31, 1 (1904).

[2] Compt. rend., 137, 660, 1061 (1903). Although the publication of Colson's article antedates mine, the latter had been written and was awaiting publication fully two months previous to the appearance of his.

[3] *Ibid.*, 139, 422 (1904).

the lead salts in metallic acetates and tartrates has been offered; the general assumption has been made that there is formed a complex ion,[1] containing lead. In a recent publication, Noyes and Whitcomb[2] have attempted to decide this question by studying the solubilities of lead sulphate in solutions of ammonium and sodium acetate and, as a result of conductivity and migration measurements, they have concluded that the increased solubility of the sulphate is due mainly to double decomposition, with the formation of unionized lead acetate. As between the suggested explanations, I have not been able to decide which the more correctly explains the increased solubility, but as a result of my own work, I am rather inclined to believe that, at least in some cases, the complex ion hypothesis more nearly represents the reaction which takes place. My previous work on lead iodide has shown that this dissolves in many of the metallic acetates with the formation of complex salts, which are either to be regarded as double salts pure and simple, or better, by assuming the intermediate formation of a complex ion, $PbC_4H_3\overset{+}{O}_2$, which is subsequently converted into the difficultly soluble complex salt. That metathesis may take place under certain conditions, I am prepared to admit, for I have found that, when lead chloride is dissolved in an aqueous or alcoholic solution of potassium or sodium acetate, the chlorides of potassium or of sodium can readily be obtained; with ammonium acetate the reaction is quite different, for in this case I obtained beautiful crystals of the compound $2PbCl_2.3NH_3$. It is evident, however, that when *lead* acetate is used as the solvent for the chloride, there can be no question of metathesis, yet the chloride of lead is distinctly more soluble in the acetate than in water. I have, moreover, succeeded in isolating some well defined products, which contain both the chloride and acetate of lead. It is possible that, with some other combination, Noyes and Whitcomb might have been led to a different conclusion.

I have found that the behavior of lead chloride toward lead

[1] Cf. Abegg and Herz: "Chemisches Praktikum," p. 68. Bailey and Cady: "Qualitative Analysis," p. 119. Kahlenberg and Shreiner: Z. physik. Chem., 17, 577.
[2] J. Am. Chem. Soc., 27, 747 (1905).

acetate is markedly influenced by the nature of the solvent used; thus, in a glacial acetic acid solution of lead acetate, the chloride dissolves, forming characteristic crystals of the composition

$$PbCl_2.Pb(C_2H_3O_2)_2.C_2H_4O_2,$$

or, as I prefer to express it,

$$(PbCl.C_2H_3O_2)_2.C_2H_4O_2,$$

while in water solutions a much more complex compound, of entirely different crystal form, is produced, *viz.*:

$$PbCl.C_2H_3O_2.Pb(C_2H_3O_2)_2.\tfrac{1}{2}C_2H_4O_2.$$

The latter is readily soluble in water and can be recrystallized undecomposed from such solutions, but it is quite easily decomposed by alcohol and acetic acid, yielding lead chloride, or intermediate compounds richer in chlorine than the original, while the former, though not soluble in cold acetic acid, is stable towards it, but is rapidly decomposed by water and alcohol. Rough quantitative experiments show that there is a certain minimum ratio which must hold between the acetate and the chloride, in order that the latter may be held in solution, this being, to some extent, independent of the actual concentration. In the acetic acid solution 1 molecule of chloride requires about 15 molecules of the acetate to hold it in solution, while in water solutions only 4 molecules are needed. A considerable variation of the amount of solvent was made in each case, without affecting the result other than changing the time required for crystallization to set in.

Solution of Lead Chloride in Acetic Acid Solution of Lead Acetate.—Appreciable amounts of lead chloride, especially if freshly prepared, dissolve when brought into a hot solution of lead acetate in glacial acetic acid. The proportions used should approximate to 18 grams of the acetate for each gram of the chloride; the dilution mainly affects the time required for the crystals to separate. The following proportions were found to give a good yield within about 12 hours: Fifty grams of lead acetate in 60 to 70 cc. glacial acetic acid; the boiling solution will dissolve about 2.7 grams of lead chloride, without subse-

quent separation. The crystals obtained in this case are quite large, with sharply defined angles; they were found to be prismatic crystals monoclinic in character.

Some difficulty was experienced for a time in finding a suitable medium for washing the crystals; alcohol was tried at first, since it did not appear to act very rapidly on them, but it was found that the analytical results, especially for chlorine, did not agree very well for the several preparations, and that they were affected by the length of time of the washing, so that it was concluded that, even in the cold and with rapid washing, using the pump, alcohol was not entirely without action; this was subsequently proven to be the case. Cold, glacial acetic acid was eventually made use of for washing and found to serve admirably, as there was practically no decomposition. Water decomposes the substance instantly. The general method of purification was to drain off the mother liquor by the aid of a pump, using a Witt filter, then wash thoroughly with glacial acetic acid, and place in a desiccator, over quicklime, for the removal of the excess of acetic acid.

It was discovered during the investigation that, in drying over lime, some difference was obtained if the substance was in the powdered condition, instead of the original coarse crystals, and that this difference was due, probably, to the loss of some acetic acid of crystallization after powdering. This was tested by drying some of the original crystals over lime for 4 days, when it was found that no odor of acetic acid could be detected. A portion of the crystals was powdered by grinding in an agate mortar, and the powdered portion then divided into two parts, the one was subjected to immediate analysis, the other replaced, together with the unpulverized substance, in the desiccator over lime. The odor of acetic acid became very pronounced upon grinding the crystals. The results of the analyses of the two portions are given below:

A.—Freshly Ground Portion.

0.1375 gram substance gave 0.1167 gram $PbSO_4$.
0.4554 gram substance gave 0.1809 gram AgCl.

0.4080 gram substance gave 0.1882 gram CO_2 and 0.0678 gram H_2O.

B.—Pulverized Portion, Kept Over Lime 3 Days Longer (No Odor).

0.0945 gram substance gave 0.0816 gram $PbSO_4$.

0.3970 gram substance gave 0.1602 gram AgCl.

0.3506 gram substance gave 0.1405 gram CO_2 and 0.0538 gram H_2O.

C.—Another Preparation, Ground and Kept Over Lime for Nearly 2 Weeks.

0.0473 gram substance gave 0.0413 gram $PbSO_4$.

0.2626 gram substance gave 0.1057 gram CO_2 and 0.0385 gram H_2O.

It was found that the original crystals could be kept for some time over lime without suffering change, although they lose acetic acid very slowly.

Numerous preparations, made under varying conditions, led to similar results, and to the conclusion that the freshly crystallized salt has a composition corresponding to the formula

$$PbCl.C_2H_3O_2.C_2H_4O_2,$$

but that it has a tendency to lose a portion of its acid of crystallization upon standing, especially when in the pulverized state. Attempts to determine the acetic acid directly, by heating, were unsuccessful; constancy of weight could not be obtained, owing probably to a deeper seated decomposition taking place.

The following tabular representation will serve to show the change occurring, due to loss of acetic acid:

	Calculated for $PbCl.C_2H_3O_2.C_2H_4O_2$.	Calculated for $PbCl.C_2H_3O_2.\frac{1}{2}C_2H_4O_2$.	Found. A.	Found. B.	Found. C.
Pb	57.25	62.43	57.96	58.97	59.63
Cl	9.81	10.69	9.82	9.98	. .
C	13.28	10.86	12.58	10.92	10.98
H	1.95	1.52	1.86	1.72	1.64

Carius[1] has described a compound similar to the above, but

[1] Ann. Chem. (Liebig), **129**, 87 (1863).

without acetic acid of crystallization, which he prepared by heating a mixture of ethylene chloride, lead acetate and acetic acid, in a sealed tube, at 180°. I have made numerous efforts to prepare the substance by Carius' method, but have in no case obtained a compound which did not consist mostly of lead chloride. Neither was I able to confirm his statement that the salt, when treated with water, is decomposed first to a white powder, which gradually goes into solution, forming a complex salt soluble in water. I found that water effects an instant and complete decomposition of the substance, forming lead chloride, but could detect no subsequent tendency for this to redissolve.

The Salt Formed in Aqueous Solution of Lead Acetate.— Carius[1] has already shown that lead chloride dissolves in an aqueous solution of lead acetate, forming a crystalline compound, to which he ascribed the formula

$$PbCl.C_2H_3O_2.Pb(C_2H_3O_2)_2.3H_2O.$$

It is quite probable, from the method of procedure described, that the product obtained by him was somewhat impure, hence it was decided to repeat the experiments.

Roughly quantitative measurements indicate that 1 molecule of lead chloride requires 4 molecules of lead acetate to effect its solution, and that this ratio is not materially affected by using, instead of water, dilute alcohol, 60–70 per cent. In practice it has been found that water containing a little acetic acid serves best as solvent and that the following proportions give the quickest separation of crystals and the best yield: One hundred cc. water, 1–2 cc. acetic acid, 25–27 grams lead acetate and 5 grams lead chloride, the solution taking place at the boiling temperature. Under these conditions there is no separation of lead chloride upon cooling, and the crystals of the substance formed separate out as a thick mass, consisting of radiating tufts of fine, silky needles. The conditions of formation were varied for the different preparations within quite wide limits, without affecting the result.

The crystals are quite easily soluble in cold water, but if the

[1] *Loc. cit.*

solution is made too concentrated some decomposition ensues, with precipitation of lead chloride. I have usually purified the substance for purposes of analysis by draining off the mother liquor as completely as possible by means of the pump, washing rapidly with several portions of cold water, then recrystallizing it by dissolving the solid in cold water, containing a drop of acetic acid,[1] to make a dilute solution. This solution was allowed to evaporate slowly over strong sulphuric acid until the crystals began to appear. Occasionally lead chloride in small amount separated out, especially if the original solution was too concentrated, this was filtered off. The crystals obtained in this way are very long, but of too small cross-section to permit of a determination of their crystal form. The following will serve as a typical analysis of a doubly recrystallized salt, dried *in vacuo*, over sulphuric acid:

0.0707 gram substance gave 0.0646 gram $PbSO_4$ = 62.40 per cent Pb.

0.3311 gram substance gave 0.0744 gram AgCl = 5.55 per cent Cl.

0.2710 gram substance gave 0.1051 gram CO_2 = 10.58 per cent C.

0.2710 gram substance gave 0.0454 gram H_2O = 1.88 per cent H.

A number of preparations and analyses were made with the object of definitely determining which of the three following possible formulas is to be ascribed to the salt, *viz.*:

	I. $PbCl.C_2H_3O_2$. $Pb(C_2H_3O_2)_2.H_2O$.	II. $PbCl.C_2H_3O_2$. $Pb(C_2H_3O_2)_2.2H_2O$.	III. $PbCl.C_2H_3O_2$. $Pb(C_2H_3O_2)_2.\frac{1}{4}C_2H_4O_2$.
Pb	64.22	62.47	63.04
Cl	5.50	5.35	5.40
C	10.70	10.87	12.81
H	1.71	1.98	1.69

It will be seen that, with the exception of the lead in I. and the carbon in III., there is very little difference in the percentages required for the three, the difference, in no case, being sufficient

[1] Water alone may be used, but unless freshly boiled, the carbon dioxide presen will produce a cloudiness, which is prevented by the use of acetic acid.

to allow of a positive decision between them based upon analysis. In the table below are given the individual determinations of the several constituents, together with the mean value in each case. These represent a number of different preparations:

Pb.	Cl.	C.	H.		Mean value.
62.80	5.61	10.53	1.73	Pb	63.05
62.85	5.60	10.47	1.85	Cl	5.56
63.25	5.64	10.58	1.88	C	10.70
63.51	5.55	10.82[1]	1.52[1]	H	1.71
62.72	5.53	11.12[1]	1.57[1]		
63.15	5.44				

From the values obtained, it is not definitely certain which of the three proposed formulas is to be ascribed to the salt. An attempt at drying, with the object of determining by loss the amount of water or of acetic acid of crystallization, led to no very satisfactory result. The sample lost 5.13 per cent in weight after drying for 6 hours at 104°, but absolute constancy of weight could not be obtained, although the loss, after drying for 3 hours, was very slow. This is contrary to the experience of Carius,[2] who states that the water of crystallization could be easily determined by drying at 100°. Assuming the loss found, *viz.*, 5.13 per cent., to be approximately correct, this might equally well be taken as proving either Formula II. or III., the first of these requiring a loss of 5.44 per cent, the latter 4.56 per cent. One sample which had stood for nearly 3 months in a desiccator, over concentrated sulphuric acid, gave, upon analysis, 5.55 per cent of chlorine and 1.52 per cent of hydrogen, thus showing that no very marked loss of water, or of acetic acid, takes place under these conditions.

Since the compound is readily soluble in water, an attempt was made to solve the problem of its formula, as well as that of similarly constituted compounds, by making a molecular weight determination, using the freezing point method. The results are given below. I., II. and III. here refer to separate preparations of the salt:

[1] These results were obtained with a sample that had been kept in a desiccator, over sulphuric acid, for several months; it may have suffered slight change.

[2] *Loc. cit.*

Solvent Water—Molecular Lowering 1850.

	Weight of substance. Gram.	Weight of water. Grams.	Freezing point of water.	Freezing point of solution.	Depression.	Molecular weight.
I.	0.1611	14.81	2°.286	2°.162	0°.124	162.3
	0.1979	"	"	2°.135	0°.151	163.7
II.	0.1065	12.93	4°.227	4°.136	0°.091	167.4
III.	0.1317	12.77	4°.383	4°.273	0°.110	173.4

The molecular weight found, 166.7 (average), being very nearly one-fourth that required for any one of the proposed formulas, may be regarded either as indicating a resolution of the substance into 4 simpler molecules or ions, *i. e.*, indicating dissociation, or that the lowering is caused entirely by lead acetate, mol. wt. = 162.4. The latter assumption, if true, might be taken as indicating the correctness of Formula III., for this can really be considered as consisting of 2 molecules of lead acetate plus 1 atom of chlorine, the additional weight of which would probably not be detected by this method of determining molecular weights.

On looking through the literature, I found one other salt of similar composition which is soluble. This is the calcium acetochloride, $CaCl.C_2H_3O_2.5H_2O$, which has been described by Fritsche.[1] I prepared the salt according to his directions, and obtained it in beautiful crystals, the analysis of which agreed well with the formula. This substance is easily soluble in water, and with it I made three molecular weight determinations, which gave 89, 85 and 87, respectively. This is approximately one-half of that required for a compound of the above formula. Here again it appears that, in water solution, some sort of dissociation takes place, the nature of which is not quite clear.

The molecular weight determinations of the salt have, therefore, not been of such character as to enable me to decide definitely what its true formula is, but they point, perhaps, more towards the correctness of the formula which has acetic acid of crystallization. It may be that, later, some more suitable solvent can be found, in which no dissociation takes place and in which the molecular weight can be definitely determined.

[1] Pogg. Ann., **28**, 121 (1833).

The salt is, as stated, soluble in cold water, but decomposes to a considerable extent in hot water; cold alcohol exerts a slow decomposing action, hot alcohol a much more rapid decomposition, both, apparently, extracting lead acetate, leaving a crystalline residue richer in chlorine. In one case, after extracting with hot alcohol, it was found that the residue contained 13.64 per cent of chlorine, which, after a second extraction, was found to have increased to 19.89 per cent. When the alcohol has dissolved enough of the acetate to bring the ratio between it and lead chloride up to the required amount, some of the latter dissolves, for it was found that, by evaporating the filtrate, a salt of the original composition was obtained. Acetic acid is very much more active than alcohol, producing instantaneous decomposition, with precipitation of lead chloride. Melting point determinations were unsatisfactory, the substance softens at 83°, but does not melt to a transparent liquid until a temperature of about 193° has been reached. There is some darkening of the mass at this point and gas is evolved, showing decomposition.

Summary.

1. A study of two complex salts containing chlorine has been made; one of these is produced when lead chloride is dissolved in a hot acetic acid solution of lead acetate; the other by use of a water solution of the acetate.

2. The probable formulas deduced for these, based upon analyses, are, respectively:

$$PbCl.C_2H_3O_2.C_2H_4O_2 \quad \text{and} \quad PbCl.C_2H_3O_2.Pb(C_2H_3O_2)_2,$$

the latter crystallizing either with water or acetic acid of crystallization.

3. The results indicate, therefore, that the nature of the solvent plays an important part in determining the composition and character of the salt formed. This appears to be one influencing the complexity, or association of the molecules, rather than the nature of the reaction, which is of the same general character in both solvents.

4. Molecular weight determinations of the second compound

mentioned above gave values approximately one-fourth the molecular weight calculated, indicating a probable dissociation; the same was found to be true for the compound $CaCl.C_2H_3O_2.5H_2O$, which has been previously described by Fritsche.

5. Lead chloride forms compounds with lead acetate analogous to those previously described for the iodide, but its action towards the alkaline acetates is quite different, the chloride undergoing double decomposition in solutions of these, the iodide, on the other hand, combining with them in the same manner as with the lead acetate.

ROSE POLYTECHNIC INSTITUTE,
TERRE HAUTE, Oct., 1905.

A STUDY OF THE REACTIONS INVOLVED IN THE FORMATION OF CERTAIN COMPLEX SALTS OF LEAD.

BY JOHN WHITE AND J. M. NELSON.

It has been previously shown by White[1] that certain difficultly soluble salts of lead, such as the iodide, chloride, etc., are soluble, to a remarkable degree, in aqueous or alcoholic solutions of metallic acetates. In offering an explanation of this fact, White assumed that the salts of lead, like those of a number of other bivalent metals, ionize in two stages, the first stage taking place more readily than the second in solutions of moderate concentration. Through the action of other salts, *e. g.*, the metallic acetates, during the first stage, it is possible to conceive of the formation of a mixed salt of the type $PbX.C_2H_3O_2$. As a proof of this view, a number of salts referable to this type have been prepared, by dissolving the halogen salts of lead in solutions of the metallic acetates.

Carius[2] has described several salts of the simple type mentioned above, but in the course of the work carried out by White, it was observed that the tendency has been rather to form salts somewhat more complex than that. This was especially the case with the iodides, and the experiments de-

[1] THIS JOURNAL, 31, 1 (1904). Cf. preceding article.
[2] Ann. Chem. (Liebig), 86, 234 (1845).

scribed in the present paper were undertaken for the purpose of studying the reactions somewhat more closely with the hope of obtaining additional information upon the subject. The object being the preparation, if possible, of the simple compound $PbI.C_2H_3O_2$, it was thought that this might be the more easily accomplished by the use of the method described by Carius, *viz.*, by heating together mixtures of lead acetate and an alkyl iodide, using a suitable solvent. It was soon discovered that the nature of the solvent had to be taken into account, as the reactions do not proceed in the same way in solvents that are markedly different in general properties.[1] Glacial acetic acid was first used, this being the solvent employed by Carius; the present paper deals more especially with reactions in this solvent.

Numerous repetitions of the experiments of Carius, following the conditions stated by him, *viz.*, with ethyl iodide and lead acetate, mixed in the proportion of 1 molecule of each, dissolved in 1 molecule of acetic acid and heated in a bomb-oven to 140°, have resulted always in failure, lead iodide being, in every case, the principal product. A study of the conditions has led to the conclusion that a larger amount of lead acetate is needed at this temperature to prevent the formation of the iodide, and that, at much lower temperatures, a reaction takes place, with the production of complex salts closely allied to the compound $PbI.C_2H_3O_2$. This compound itself has not yet been obtained. We believe the reason to be either the greater ease of decomposition of the iodine salts or the greater reactivity (more ready ionization) of the iodine compounds, because, in the preceding paper, it has been shown that the chlorine compound probably exists.

Instead of using the bomb-oven as described by Carius, we have found it more convenient to carry out the reactions described in this article by heating the requisite amount of lead acetate, alkyl iodide and acetic acid, enclosed in a short sealed tube, bound to the axle of a rotating device within a water-bath. In this way the contents of the tube could be kept constantly stirred, a necessary precaution, because it was found

[1] *Vide* preceding paper.

that it serves in large measure to prevent the formation of lead iodide, while at the same time it served as a stirrer for the water in the bath.

The results showed that the reaction which takes place under these conditions is of a somewhat complex character, and that its exact nature could not be determined. Something was, however, learned regarding the influences operating to produce the reaction and, incidentally, sufficient information was acquired to permit us to draw certain inferences regarding its general trend. This will appear in the experimental work following. The temperature is an important factor, as was to be expected, since it influences the degree of dissociation and, consequently, the active mass of the dissolved substances, which are also, to some extent, although not so markedly, affected by varying the relative proportions of the solvent and of the reacting substances.

Contrary to our hope that we might obtain the lead acetoiodide only, we found that the principal product is a complex salt of the general character of those previously described by White and corresponding to the hypothetical formula,

$$(PbI.C_2H_3O_2)_5.Pb(C_2H_3O_2)_2.$$

The formation of such a salt may be explained theoretically in one of two ways, represented by the following sets of equations:

I. (*a*) $Pb(C_2H_3O_2)_2 = PbC_2H_3\overset{+}{O}_2 + C_2H_3\overset{-}{O}_2$;

(*b*) $PbC_2H_3\overset{+}{O}_2 + C_2H_3\overset{-}{O}_2 + C_2H_5I = PbI.C_2H_3O_2 + C_2H_3O_2C_2H_5$;

(*c*) $5PbI.C_2H_3O_2 + Pb(C_2H_3O_2)_2 = (PbI.C_2H_3O_2)_5.Pb(C_2H_3O_2)_2$.

II. (*a*) $Pb(C_2H_3O_2)_2 + 2C_2H_5I = PbI_2 + 2C_2H_5.C_2H_3O_2$;

(*b*) $xPbI_2 + (x+1)Pb(C_2H_3O_2)_2 = (PbI.C_2H_3O_2)_{2x}.Pb(C_2H_3O_2)_2$.

The result is, naturally, the same in either case, although the intermediate stages vary considerably. It was in the endeavor to decide between these that the experiments described

below were undertaken. The general result seems to be rather in favor of the first set of reactions. It is certain that, under suitable conditions, a white, crystalline salt can be obtained directly and without any indications of an intermediate formation of lead iodide, thus pointing to the correctness of the first set of reactions. Moreover, in those instances where lead iodide was formed, the conditions were such as to favor the decomposition of the unstable compound, $PbI.C_2H_3O_2$, assuming it to be the first product of the reaction, into the iodide and acetate of lead.

The facts observed during the course of the investigation seem to be in harmony with this assumption. Such being the case, the following may serve as an explanation of what was observed to take place during the several experiments to be described below:

The temperature must, of necessity, exert a marked effect upon the reaction, for an increase of temperature would naturally increase the tendency of both reactions, (*a*) and (*b*), to take place, since it would produce an increase in the degree of dissociation of the lead acetate,[1] and likewise in the reactivity of the alkyl halide.[2] At the same time this increase in temperature would have a marked tendency to cause a decomposition of the rather unstable substance $PbI.C_2H_3O_2$, forming lead iodide (*vide* Exps. 1 and 2). This formation of lead iodide could only be prevented by increasing the amount of lead acetate, so as to cause the removal of the iodine from the solution in the form of the difficultly soluble salt,

$$(PbI.C_2H_3O_2)_2.Pb(C_2H_3O_2)_2.$$

It is, therefore, to be expected that for a given initial amount of the reacting substances, there is a certain maximum, beyond which the temperature cannot be raised, without giving rise to the formation of lead iodide. This is in entire accord with our observations.

An increase in the amount of alkyl halide, or a decrease in

[1] It is probably in connection with this that the nature of the solvent has to be taken into account, since this would naturally have an effect upon the dissociation of the lead salt.

[2] Slator (J. Chem. Soc., 85, 1286 (1904)) has shown that the effect of temperature is very marked, a rise of 10° trebles the velocity of the reaction.

the amount of lead acetate, would, according to the law of mass action, tend to increase the amount of acetoiodide formed and, in the absence of a sufficient excess of lead acetate, also the decomposition of this into lead iodide (*vide* Exps. 6 and 7). For a given temperature the particular alkyl halide used will also, in a measure, determine whether or not the iodine will stay in the solution or be precipitated as lead iodide; ethyl iodide, for instance, being considerably less reactive at a given temperature than methyl iodide,[1] may be used at higher temperatures than the latter without giving rise to the formation of lead iodide (*vide* Exps. 8 and 9).

Increasing the amount of the solvent acetic acid would affect the trend of the reaction in several ways; it would decrease the concentrations and, consequently, the active masses of the reacting substances and, unless this effect were equal in degree for both, the whole reaction would be affected; in addition, the increase in solvent would have a marked decomposing effect upon the acetoiodide formed, tending, therefore, to the formation of lead iodide[2] (*vide* Exps. 3, 4 and 5).

It is, of course, not impossible to interpret the results in such a way as to make them conform to the set of reactions designated as II. No very definite proof can be furnished indicating which of the sets of reactions is to be regarded as the correct one, but the facts are so easily explained by the former set that we feel inclined, in the absence of contrary evidence, to accept this in preference to the other.

EXPERIMENTAL.

Preparation of the Salt, $(PbI.C_2H_3O_2)_2.Pb(C_2H_3O_2)_2$.—Six grams of methyl iodide, 12 grams of lead acetate, about 1 molecule of each, 4 cc. of acetic acid and 4 cc. of acetic anhydride[3] were brought together in a sealed tube. After heating at 98°, for an hour, a white, crystalline substance began to separate. The heating was continued at the same temperature for about 7 hours, the tube was then removed from the

[1] Slator: *Loc. cit.*

[2] *Vide* White's "Experiments with the Iodides," *loc. cit.*

[3] The lead acetate not being completely dehydrated, a little acetic anhydride was added to take up the water and prevent the formation of basic iodide.

bath and opened, the crystals filtered upon a Witt plate and examined under the microscope; they appeared homogeneous throughout and were monoclinic. They were washed with cold alcohol, which does not exert a very rapid decomposing action upon them and then dried in a partial vacuum, over concentrated sulphuric acid. Analysis:

	Calculated for $(PbI.C_2H_3O_2)_2.Pb(C_2H_3O_2)_2$.	Found.
Pb	54·23	53·94
I	27·71	27·53
C	7·34	7·18
H	0.92	0.88

Preparation 2.—The proportions were the same as in the first preparation; the temperature was, however, considerably lower, 70° instead of 98°. After 4 hours, lead iodide began to form. The tube was opened, the liquid filtered from the lead iodide and poured into a flask, which was then allowed to stand on a steam radiator for about 10 hours, after which time white crystals formed at the bottom of the flask, with a ring of lead iodide around the flask at the top of the liquid. The crystals, which were quite large, were removed from the flask mechanically and were washed and dried as in the previous case. Analysis:

	Calculated for $(PbI.C_2H_3O_2)_2.Pb(C_2H_3O_2)_2$.	Found.
Pb	54·23	53·98
I	27·71	27·37
C	7·34	7·43
H	0.92	0.89

Preparation 3.—Six grams of methyl iodide (1 mol.), 10 grams of lead acetate (0.75 mol.), 6 cc. of acetic acid and 2 cc. of acetic anhydride were heated as in the preceding preparations. The temperature of the bath was kept between 60° and 70°. After 6 hours a very good crop of white crystals had separated; they were removed from the tube and showed, under the microscope, the same crystal form as those obtained in the previous preparations. No lead iodide was observed in this case during the reaction. The crystals were washed with alcohol and dried over sulphuric acid for analysis:

	Calculated for $(PbI.C_2H_3O_2)_2.Pb(C_2H_3O_2)_2$.	Found.
Pb	54.23	54.55
I	27.71	27.35
C	7.34	7.13
H	0.92	0.92

Having thus demonstrated the existence of a definite compound, as shown by the analysis of the various preparations, the following set of experiments were undertaken with the object of making a closer study of the causes operating to influence the trend of the reaction:

Influence of Temperature.

Exp. 1.—Six grams of methyl iodide, 6 grams of lead acetate, molecular proportions 2 : 1, 2 cc. of acetic acid and 2 cc. of acetic anhydride were used. The temperature of the bath was maintained at 85°. The solution remained clear for about 3 hours, when the formation of lead iodide began.

Exp. 2.—The same amounts of substances were used as in the preceding case, but the temperature was 70°. The solution remained clear for about 2 hours, when the white crystals began to deposit.

It appears, from the above, that the temperature has a marked effect upon the reaction and that for these proportions of the reacting substances it must not be allowed to exceed 70°–75°, if it is desired to prevent the formation of lead iodide. When other proportions were used similar results were obtained.

Influence of Acetic Acid.

Exp. 3.—Six grams of methyl iodide, 12 grams of lead acetate, molecular proportion 1 : 1, 16 cc. of acetic acid and 4 cc. of acetic anhydride, were heated for 2.5 hours, at about 85°–90°. Lead iodide was formed toward the latter part of the operation.

Exp. 4.—Six grams of methyl iodide, 12 grams of lead acetate, molecular proportion 1 : 1, 12 cc. of acetic acid and 4 cc. of acetic anhydride were used. The temperature was 85°–90°. Lead iodide began to form after about 3 hours.

Exp. 5.—Six grams of methyl iodide, 12 grams of lead acetate, molecular proportion 1 : 1, 4 cc. of acetic acid and 4 cc. of acetic anhydride were heated to 98°. No lead iodide was formed, instead only the white, crystalline salt.

It appears that, for a given proportion of the other constituents and at a certain temperature, there is a limit to the amount of acetic acid which can be used, if the complex salt is desired.

Influence of Lead Acetate.

Exp. 6.—Six grams of methyl iodide, 6 grams of lead acetate, molecular proportion 2 : 1, 2 cc. of acetic acid and 2 cc. of acetic anhydride were maintained at 85°, for 3 hours, when the formation of lead iodide was observed.

Exp. 7.—Six grams of methyl iodide, 12 grams of lead acetate, molecular proportion 1 : 1, 4 cc. of acetic acid and 4 cc. of acetic anhydride were heated at 98°. No lead iodide separated out, instead only the white salt. It will be observed that, in this case, the proportion of acetic acid had been increased, also the temperature, which would both tend to the production of lead iodide, but the increase in the proportion of the acetate more than offset this tendency. The two experiments, taken together, show that lead acetate, when in sufficient excess, has a very strong influence in preventing the formation of lead iodide.

Influence of Alkyl Halide.

Exp. 8.—Six grams of methyl iodide, 6 grams of lead acetate, molecular proportion 2 : 1, 8 cc. of acetic acid and 2 cc. of acetic anhydride were heated at 70° for a short time, when lead iodide was formed.

Exp. 9.—Six grams of ethyl iodide, 6 grams of lead acetate, molecular proportion 2 : 1, 8 cc. of acetic acid and 2 cc. of acetic anhydride were heated at 70°, for some time. No lead iodide was formed, the white salt being obtained instead.

In this case it is evident that the methyl iodide, being more active at a given temperature than ethyl iodide, is more likely to cause the formation and separation of lead iodide.

Summary.

1. A new salt of the same general character as those previously described has been prepared and studied. This salt, however, is different in composition and, to some extent, in properties, from that previously obtained by dissolving lead iodide in an acetic acid solution of lead acetate.

2. The simple compound $PbI.C_2H_3O_2$ could not be obtained.

3. It has been found that the reaction is influenced by changes of temperature, concentration and the relative proportions of the reacting substances.

4. From this it is possible to gain some insight into the nature of the reaction. While not definitely proven, all the facts observed apparently point to the conclusion that an intermediate compound, $PbI.C_2H_3O_2$, is formed.

Up to the present time the following salts have been obtained:

Simple salt.	Molecular proportions.
	1 : 1
$PbCl.C_2H_3O_2$	$PbCl.C_2H_3O_2.Pb(C_2H_3O_2)_2.\frac{1}{2}C_2H_4O_2$
	$PbI.C_2H_3O_2.Pb(C_2H_3O_2)_2.\frac{1}{2}C_2H_4O_2$
	$PbI.C_2H_3O_2.NaC_2H_3O_2.\frac{1}{2}C_2H_4O_2$
	Without acetic acid.
	$PbI.C_2H_3O_2.KC_2H_3O_2$
	$PbI.C_2H_3O_2.NH_4C_2H_3O_2$
	More complex salts.
	$PbI.C_2H_3O_2.(NaC_2H_3O_2)_2.\frac{1}{2}C_2H_4O_2$
	$(PbI.C_2H_3O_2)_2.Pb(C_2H_3O_2)_2$

The bromine compounds are at present under investigation, and it is the intention to take up the sulphate, and possibly some others, in the near future.

ROSE POLYTECHNIC INSTITUTE,
TERRE HAUTE, Oct., 1905.

THE DOUBLE SALTS OF MERCURIC CHLORIDE WITH THE ALKALI CHLORIDES AND THEIR SOLUBILITY.

By H. W. Foote and L. H. Levy.

In a previous article by one of us,[1] the double caesium mercuric chlorides were determined by what we shall call the solubility method and found to be the same as those described by Wells.[2] The advantages of the method we used are that all stable salts, forming at a given temperature, can be determined with a good degree of certainty and that the solubility conditions under which each salt forms are ascertained. The method has already been applied to several series of double salts besides the caesium mercuric chlorides.[3] The method used in the present article is essentially the same that has been used before. Varying mixtures, carefully weighed, of mercuric chloride and an alkali chloride were treated with hot water enough to dissolve them, placed in the thermostat at 25° and shaken, usually for several days. Weighed quantities of solution were then removed through a filter of glass wool and analyzed. The residues were dried as quickly as possible between filter paper and analyzed by the same method used for the solutions.

The analyses were carried out by precipitating mercuric sulphide from the solution acidified with hydrochloric acid, filtering on a Gooch crucible, drying at 100° and weighing the mercuric sulphide. The filtrate from the sulphide was evaporated and the residue weighed as chloride.

A series of two or more results giving a constant composition of the residue and varying solubility shows a pure double salt to be present, while constant solubility and varying residue indicates a mixture of two salts.

POTASSIUM MERCURIC CHLORIDES.

By H. W. Foote.

Three double potassium mercuric chlorides have been de-

[1] This Journal, 30, 339.
[2] Am. J. Sci., 44, 221 (1892).
[3] This Journal, 30, 330; 32, 246, 251; 34, 153, 164.

scribed by Bonsdorf[1] and we have found the same ones at 25°. These salts are :

$$2KCl.HgCl_2.H_2O;$$
$$KCl.HgCl_2.H_2O;$$
$$KCl.2HgCl_2.2H_2O.$$

The results obtained are given below. Constant composition of the residues, showing a pure double salt, is italicized. The solubility of pure potassium chloride was determined by Mr. J. G. Statiropoulos in duplicate from two solutions, one of which was first supersaturated and the other undersaturated, at 25°.

The analyses of the residues in Nos. 10–14 vary considerably, although the pure 1 : 1 salt was present. This was because the salt crystallized as a mass of silky needles which it was impossible to dry properly.

SODIUM MERCURIC CHLORIDES.

BY H. W. FOOTE.

Two sodium mercuric chlorides have been described by Bonsdorf[2] and others. They have the formulas :

$$2NaCl.HgCl_2;$$
$$NaCl.HgCl_2.2H_2O.$$

We have been unable to detect the first salt at either 25° or 10°.3.

The results obtained at 25° are given in Table II.

The results show clearly that the salt $NaCl.HgCl_2.2H_2O$ is present, but show no indication of $2NaCl.HgCl_2$. The latter salt contains 69.84 per cent of mercuric chloride. Had this salt formed, the solubility results in Nos. 1–3 of the following table, corresponding in composition to a mixture of NaCl and the 2 : 1 compound would have been different from the solubility in No. 4, corresponding to a mixture of 2 : 1 and 1 : 1 derivatives. That the results are the same shows that this salt has not been produced, but that the residues in the four results consist of a mixture of the same salts.

[1] Pogg. Ann., 17, 115.
[2] *Loc. cit.*

Table I.—Solubility of Potassium and Mercuric Chlorides at 25°.

No.	Per cent KCl in solution.	Per cent $HgCl_2$ in solution.	Per cent KCl in residue.	Per cent $HgCl_2$ in residue.	Per cent H_2O in residue.	Residue contains :
0	26.46	none	100	none		KCl
1	26.24	15.04	. .	3.63	. .	KCl and $2KCl.HgCl_2.H_2O$
2	26.43	15.02	. .	26.15	. .	
3	26.33	15.02	. .	52.01	. .	
4	26.33	14.92	. .	61.04	. .	
5	23.74	18.91	*34.61*	*61.66*	*3.73*	$2KCl.HgCl_2.H_2O$
6	22.36	21.39	*34.77*	*62.02*	*3.21*	
7	21.39	23.88	*34.80*	*61.85*	*3.35*	
	Calculated for $2KCl.HgCl_2.H_2O$,		34.05	61.84	4.11	
8	20.32	27.62	. .	65.24	. .	$2KCl.HgCl_2.H_2O$ and $KCl.HgCl_2.H_2O$
9	20.26	27.38	. .	73.98	. .	
10	17.85	25.34	*21.89*	*75.10*	*3.01*	$KCl.HgCl_2.H_2O$
11	9.26	18.95	*21.02*	*73.36*	*5.62*	
12	7.80	19.56	*20.76*	*73.06*	*6.18*	
13	6.84	22.81	*20.75*	*74.54*	*4.71*	
14	6.66	24.32	*20.54*	*73.99*	*5.47*	
	Calculated for $KCl.HgCl_2.H_2O$,		20.52	74.53	4.95	
15	6.52	25.13	. .	76.46	. .	$KCl.HgCl_2.H_2O$ and $KCl.2HgCl_2.2H_2O$
16	6.64	25.16	. .	80.60	. .	
17	6.27	25.11	*12.09*	*83.20*	*4.71*	$KCl.2HgCl_2.2H_2O$
18	5.77	24.73	*11.87*	*83.18*	*4.95*	
	Calculated for $KCl.2HgCl_2.2H_2O$,		11.43	83.05	5.52	
19	4.68	24.75	. .	84.46	. .	$KCl.2HgCl_2.2H_2O$ and $HgCl_2$
20	4.66	25.17	. .	93.68	. .	
21	4.69	24.82	. .	98.50	. .	
22	none	6.90	none	100.00	none	$HgCl_2$

Table II.—Solubility of Sodium and Mercuric Chlorides at 25°.

No.	Per cent NaCl in solution.	Per cent $HgCl_2$ in solution.	Per cent NaCl in residue.	Per cent $HgCl_2$ in residue.	Per cent H_2O in residue.	Residue contains:
0	26.50	none	100.00	none		NaCl
1	18.66	51.35	. .	16.36	. .	NaCl and $NaCl.HgCl_2.2H_2O$
2	18.71	51.32	. .	21.98	. .	
3	18.64	51.42	. .	65.42	. .	
4	18.87	51.26	.	71.25	. .	
5	14.97	57.74	*16.38*	*74.18*	*9.44*	$NaCl.HgCl_2.2H_2O$
6	14.03	59.69	*16.36*	*74.21*	*9.43*	
7	13.25	62.16	*16.16*	*74.70*	*9.14*	
8	13.17	62.59	*15.96*	*74.76*	*9.28*	
	Calculated for $NaCl.HgCl_2.2H_2O$,		16.01	74.14	9.85	
9	12.97	62.50	. .	78.20	. .	$NaCl.HgCl_2.2H_2O$ and $HgCl_2$
10	13.14	62.48	. .	88.64	. .	
11	13.15	62.55	. .	90.83	. .	

It was thought possible that the 2 : 1 salt might form at a lower temperature and two solubility determinations were accordingly made at 10°.3. The mixtures were so chosen that, after saturation had taken place, the composition of the residues would correspond in one case to a mixture of sodium chloride and the 2 : 1 salt, and in the other to a mixture of the 2 : 1 and 1 : 1 compounds. The solubility apparatus was kept at 10°.3 by means of a cold water thermostat.[1] The results obtained were as follows :

Table III.—Solubility of Mixtures of Sodium and Mercuric Chlorides at 10°.3.

	Per cent NaCl in solution.	Per cent $HgCl_2$ in solution.	Per cent NaCl in residue.	Per cent $HgCl_2$ in residue.	Per cent H_2O in residue.
1	19.46	46.49	67.46	29.19	3.35
2	19.48	46.50	22.83	68.85	8.32
	$2NaCl.HgCl_2$ contains		30.16	69.84	none

The solubility is the same in the two experiments. The ratio of Na : Hg in the first residue is 10.7 : 1 and in the second 1.53 : 1. It follows that the same salts were present in both residues and that the 2 : 1 salt does not form. Had this salt formed, the solubility in the two experiments must have been different. It will be noticed, also, that both residues contain water of crystallization. We conclude from our results that the 2 : 1 salt which was described by Bonsdorf does not exist between 10°.3 and 25° and that he must have obtained mixtures of NaCl with the 1 : 1 salt.

RUBIDIUM MERCURIC CHLORIDES.

By H. W. Foote and L. H. Levy.

Godeffroy described the following double rubidium mercuric chlorides :[2]

$2RbCl.HgCl_2$;

$2RbCl.HgCl_2.2H_2O$;

$RbCl.HgCl_2$.

For our experiments pure rubidium chloride was obtained from rubidium alum which contained some potassium. It was

[1] Z. physik. Chem., 33, 749.

[2] Arch. der Pharm., [3], 12, 47.

partially separated from the potassium alum by repeated fractional crystallization and finally precipitated as Rb_2PbCl_6. The spectroscope showed no trace of caesium or potassium. This work was done by one of us (Levy) under the direction of Professor H. L. Wells, to whom our thanks are due.

The solubility results obtained are given in Table IV. As before, constant residues showing double salts are italicized.

From the constant residues in the above table it will be seen that, at 25°, there exist 5 double rubidium-mercury chlorides with the following formulas:

(1) $RbCl.5HgCl_2$;
(2) $3RbCl.4HgCl_2.H_2O$;
(3) $RbCl.HgCl_2.H_2O$;
(4) $3RbCl.2HgCl_2.2H_2O$;
(5) $2RbCl.HgCl_2.H_2O$.

None of these have the composition given by Godeffroy, although the double salt $2RbCl.HgCl_2.H_2O$ lies between Godeffroy's double salts, $2RbCl.HgCl_2$ and $2RbCl.HgCl_2.2H_2O$. That the double salt $2RbCl.HgCl_2.H_2O$ is stable at ordinary temperatures was shown when crystals, which had separated from a solution containing unknown amounts of rubidium and mercuric chlorides, were analyzed.

	RbCl.	$HgCl_2$.	H_2O.
I.	45.65	51.10	3.25
II.	45.25	51.18	3.57
Calculated for $2RbCl.HgCl_2.H_2O$.	45.55	51.05	3.40

These crystals were large and well defined.

The double salt $3RbCl.4HgCl_2.H_2O$ is an unusual type of an alkali halide double salt. To verify its existence, some of it was allowed to crystallize slowly in the thermostat at 25°, the crystals were separated from the mother liquor and dried in a room heated to 25°. Analysis:

	RbCl.	$HgCl_2$.	H_2O.
Found	25.32	73.39	1.29
Calculated for $RbCl.4HgCl_2.H_2O$	24.76	74.01	1.23

Table IV.—Solubility of Rubidium and Mercuric Chlorides at 25°.

No.	Per cent RbCl in solution.	Per cent $HgCl_2$ in solution.	Per cent RbCl in residue.	Per cent $HgCl_2$ in residue.	Per cent H_2O in residue.	Residue contains:
0	48.57	none	100.00	none	none	RbCl
1	46.76	9.18	88.04	11.24	0.72	RbCl and $2RbCl.HgCl_2.H_2O$
2	47.54	9.49	60.33	37.51	2.16	
3	47.55	9.38	56.59	40.75	2.66	
4	47.30	9.47	46.73	49.38	3.89	
5	47.65	10.35	*46.50*	*50.92*	*2.58*	$2RbCl.HgCl_2.H_2O$
6	35.16	19.58	*45.98*	*50.80*	*3.22*	
	Calculated for $2RbCl.HgCl_2.H_2O$,		45.55	51.05	3.40	
7	34.77	19.94	43.07	52.44	4.49	$2RbCl.HgCl_2.H_2O$ and $3RbCl.2HgCl_2.2H_2O$
8	34.76	20.10	41.10	55.36	3.54	
9	30.27	20.17	*39.07*	*57.34*	*3.59*	$3RbCl.2HgCl_2.2H_2O$
10	29.20	20.55	*39.10*	*57.47*	*3.43*	
11	27.38	20.63	*38.67*	*57.40*	*3.93*	
	Calculated for $3RbCl.2HgCl_2.2H_2O$,		38.55	57.62	3.82	
12	26.83	20.87	38.48	57.36	4.16	$3RbCl.2HgCl_2.2H_2O$ and $RbCl.HgCl_2.H_2O$
13	27.09	20.97	31.40	64.35	4.25	
14	26.15	20.58	*30.34*	*65.48*	*4.18*	$RbCl.HgCl_2.H_2O$
15	23.81	18.70	*30.87*	*65.10*	*4.03*	
16	18.10	14.25	*29.87*	*65.28*	*4.85*	
17	10.87	10.42	*29.33*	*66.15*	*4.52*	
	Calculated for $RbCl.HgCl_2.H_2O$,		29.49	66.11	4.40	

Table IV.—Solubility of Rubidium and Mercuric Chlorides at 25° (Continued).

No.	Per cent RbCl in solution.	Per cent $HgCl_2$ in solution.	Per cent RbCl in residue.	Per cent $HgCl_2$ in residue.	Per cent H_2O in residue.	Residue contains:
18	10.68	10.56	28.59	67.99	3.42	$RbCl.HgCl_2.H_2O$ and
19	10.50	10.05	26.22	72.20	1.58	$3RbCl.4HgCl_2.H_2O$
20	10.06	9.86	*25.28*	*73.38*	*0.84*	
21	8.48	8.71	*25.30*	*73.15*	*1.55*	
22	8.46	8.80	*25.44*	*73.67*	*0.89*	$3RbCl.4HgCl_2.H_2O$
23	5.68	8.70	*25.09*	*73.46*	*1.45*	
24	5.10	8.33	*24.92*	*73.93*	*1.15*	
	Calculated for $3RbCl.4HgCl_2.H_2O$,		24.76	74.01	1.23	
25	3.43	8.25	22.79	75.72	1.49	$3RbCl.4HgCl_2.H_2O$
26	3.38	8.00	12.68	86.74	0.58	and $RbCl.5HgCl_2$
27	2.98	7.71	*8.40*	*91.24*	. .	
28	1.89	7.64	*8.38*	*91.78*	. .	$RbCl.5HgCl_2$
29	1.50	7.55	*8.30*	*91.81*	. .	
30	1.10	7.21	*8.07*	*91.58*	. .	
	Calculated for $RbCl.5HgCl_2$,		8.20	91.80		
31	0.79	7.16	6.91	93.15	. .	$RbCl.5HgCl_2$
32	0.84	7.42	2.27	97.09	. .	and $HgCl_2$
33	none	6.90	none	100.00	. .	$HgCl_2$

The crystals of this double salt separate in a mass of silky needles, difficult to free completely from the mother liquor.

The results of Table IV. are plotted graphically in Fig. I.,

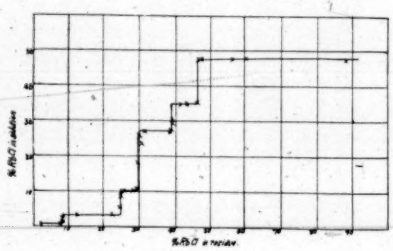


Fig. I.

the abscissa representing the percentage of rubidium chloride in the residue, and the ordinate, the percentage of the same salt in solution. The vertical lines then show constant residue and variable solubility, corresponding to pure double salt, and the horizontal lines variable residue and constant solubility, corresponding to a mixture.

It seemed of interest to compare the solubilities of the salts of the different alkali metals. For this purpose the percentage composition of the solutions was recalculated to give the molecules of mercuric chloride and of alkali chloride dissolved in 100 molecules of water. The values for the caesium mercuric chlorides previously published[1] were also recalculated. The results obtained are plotted in the diagram, Fig. II. The molecules of mercuric chloride and of alkali chloride dissolved in 100 molecules of water are plotted, respectively, as ordinate and abscissa, except in the case of sodium chloride. Here the solubility was so great that the values obtained were multiplied by one-third. Each curve is designated by the symbol of the alkali metal present. The points on the curve where two salts were present together are represented by circles; by crosses where only one salt formed.

The dotted lines radiating from the intersection of the ordi-

[1] *Loc. cit.*

nate and abscissa represent the composition of solutions formed by dissolving the different double salts in water, and the behavior of a given double salt, on recrystallizing at 25°, is deter-

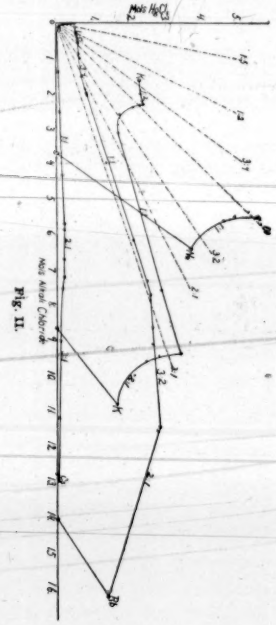


Fig. 11.

mined from the intersection of the dotted line representing its solutions with the solubility curve.[1] For instance, the composition of a solution of 1 : 1 salt is represented by some point on the dotted line, making an angle of 45° with the abscissa. This line cuts the solubility curve of the 1 : 1 salts of sodium,

[1] Van 't Hoff : Vorles. über Bild. und Spalt. von Doppelsalzen.

potassium and caesium and the curve of the 3 : 4 salt of rubidium, showing that these salts can be in equilibrium with a solution containing equal molecules of the alkali chloride and mercuric chloride. The 1 : 1 salts of sodium, potassium and caesium can, therefore, be recrystallized, while the rubidium salt first yields the 3 : 4 compound.

The behavior of the various salts, on recrystallizing, is as follows :

3 : 1.—Only the caesium salt forms. On recrystallizing, it yields the 1 : 1 type.

2 : 1.—The potassium and caesium salts yield the 1 : 1 type. The rubidium salt forms the 3 : 4.

3 : 2.—Only the rubidium salt forms. On recrystallizing it yields the 3 : 4.

1 : 1.—The sodium, potassium and caesium salts recrystallize. The rubidium salt yields the 3 : 4.

3 : 4.—Only the rubidium salt forms. It yields the 1 : 5.

1 : 2.—The potassium salt yields mercuric chloride ; the caesium salt the 1 : 1.

1 : 5.—The rubidium salt yields mercuric chloride ; the caesium salt the 1 : 2.

SHEFFIELD LABORATORY,
NEW HAVEN, CONN.,
November, 1905.

Contribution from the Chemical Laboratories of Harvard University.

ON THE ADDITION PRODUCTS OF *p*-NITROSODIMETHYLANILINE WITH CERTAIN PHENOLS.

BY HENRY A. TORREY AND J. A. GIBSON.

In an earlier paper by H. Hardenbergh and one of us[1] it was shown that quinhydrone and phenoquinone were addition products which, on solution in benzene and other neutral solvents, were dissociated into their constituent parts, namely, quinone and hydroquinone in the former and quinone and phenol in the latter case. Paranitrosodimethylaniline, which is frequently given the quinoid structure, seems to form similar compounds with certain substituted phenols. Edeleanu

[1] THIS JOURNAL, 33, 167.

and Euescu[1] have described a few bodies of this nature and we have somewhat extended the number. We have found that there is a considerable degree of analogy between phenoquinone and quinhydrone and the products from *p*-nitrosodimethylaniline. Quinone unites with 2 molecules of a monatomic phenol and 1 molecule of a diatomic, and we find this also to be true, for the most part, of *p*-nitrosodimethylaniline. Further, the compounds of the latter with 2 molecules of the phenol, in the solid state, resemble phenoquinone in color, whereas those with 1 molecule of the diatomic phenol are more nearly like quinhydrone, and just as phenoquinone and quinhydrone both dissolve with the yellow color of quinone, these derivatives of *p*-nitrosodimethylaniline dissolve with the green color of the latter body. That this is due to the dissociation of these addition products into the phenol and *p*-nitrosodimethylaniline is shown by the molecular weight determinations given below.

We shall consider first the products from monatomic phenols and then those from polyatomic phenols.

Trichlorphenol and p-Nitrosodimethylaniline.

One gram of *p*-nitrosodimethylaniline was dissolved in a very small quantity of warm benzene and was added to a concentrated benzene solution of 2 grams of trichlorphenol. No precipitation occurred immediately, but on adding ligroin the crystallization began and, after the mixture had stood for a short time, a good yield of fine, reddish crystals of the product described by Edeleanu and Euescu was obtained.[2] The product was filtered, washed with ligroin and dried in a vacuum desiccator; it melted at 91°. That the trichlorphenol used in the preparation was pure was shown by the melting-point, 67°, and an analysis. Cl required 53.92, found 53.88 per cent.

An analysis of the product of the reaction shows the percentage of chlorine required by an addition product formed from 2 molecules of trichlorphenol and 1 molecule of *p*-nitrosodimethylaniline, $ONC_6H_4N(CH_3)_2.(C_6H_2Cl_3OH)_2$.

[1] J. Chem. Soc., 70, 1, 359 (1896).
[2] *Loc. cit.*

0.2282 gram substance gave, by the sodium peroxide method,[1] 0.3582 gram AgCl.

	Calculated for $ONC_6H_4N(CH_3)_2.(C_6H_2Cl_3OH)_3$.	Found.
Cl	39.08	38.84

The body which, in the solid condition, consisted of fine, deep red crystals, dissolved in all solvents with the characteristic green color of *p*-nitrosodimethylaniline. Its solubility is as follows: Readily soluble in cold chloroform, alcohol, acetone and benzene; soluble in ether; insoluble in cold ligroin, but slightly soluble in the hot liquid.

The following molecular weight determination shows that the addition product is completely dissociated in these solvents into *p*-nitrosodimethylaniline and trichlorphenol, and that the green color is due to the free *p*-nitrosodimethylaniline, since the trichlorphenol, of course, is colorless.

The molecular weights are calculated from the well known formula $M = \frac{100\,K\,s}{W\,x}$.

In the tables the concentration is given in grams of dissolved substance in 100 grams of the solvent.

Molecular Weight of Addition Product of Trichlorphenol and of p-Nitrosodimethylaniline by the Ebullioscopic Method.

W.	*s.*	*x.*	K.	M.
100	0.5830	0.087	26.7	178
.	1.3701	0.197	.	186
.	2.0054	0.284	.	184
.	2.6837	0.401	.	179

The molecular weight is found to be one-third of the molecular weight of $ONC_6H_4N(CH_3)_2.(C_6H_2Cl_3OH)_3$, $\frac{543}{3} = 178$; this is as it should be if the dissociation is complete.

Tribromphenol and p-Nitrosodimethylaniline.

This addition product was made in a similar manner to that used for the trichlorphenol derivative, by adding 1 gram of the *p*-nitrosodimethylaniline, dissolved in 5 cc. of benzene, to 5

[1] Pringsheim: THIS JOURNAL, 31, 386.

grams of tribromphenol in 10 cc. of benzene. After standing some time, dark red crystals with a blue reflex separated in large quantities. These were collected on a filter, washed with ligroin and, after drying, were analyzed :

0.2250 gram substance gave, by the sodium peroxide method, 0.3114 gram AgBr.

	Calculated for $ONC_6H_4N(CH_3)_2.(C_6H_2Br_3OH)_2$.	Found.
Br	59.11	58.90

The analysis shows that the substance was pure.[1] The following molecular weight determination proves that the addition product is completely dissociated when dissolved in benzene.

Molecular Weight of Addition Product of Tribromphenol and p-Nitrosodimethylaniline by the Ebullioscopic Method.

W.	*s.*	*x.*	K.	M.
100	1.5740	0.160	26.7	262
.	3.7248	0.362	.	274
.	6.4259	0.590	.	290
.	8.0906	0.732	.	295
.	9.2783	0.834	.	297

Its solubilities are practically the same as those of the trichlorphenol derivative and in all cases its solutions are green.

The Addition Product of Salicylic Acid and p-Nitrosodimethylaniline.

When 2 grams of *p*-nitrosodimethylaniline, dissolved in 15 cc. of benzene, are added to 4 grams of salicylic acid, dissolved in 50 cc. of benzene, a deep orange-red, crystalline precipitate falls. This was collected on a filter, dried on a clay plate and afterwards in a vacuum desiccator. The yield of the dry substance was very good. Recrystallized from hot benzene, it gives fine, dark red needles, melting at 110°.

I. 0.2251 gram substance gave 13.9 cc. moist N at 27°.3 and 765 mm.

II. 0.4540 gram substance gave 27.1 cc. moist N at 23° and 759.5 mm.

[1] The tribromphenol used in making this preparation was also analyzed for bromine. Found, 72.48; required, 72.51 per cent.

	Calculated for $ONC_6H_4N(CH_3)_2.(HOC_6H_4COOH)_2$.	Found. I.	II.
N	6.57	6.85	6.72

The analysis and the color of the compound indicate that it is an addition product similar to those formed by the other two phenols investigated. It cannot be a *salt* of *p*-nitrosodimethylaniline, for the latter would unite with only one equivalent of the acid and, further, the product dissolves in organic solvents, such as benzene, with a green color. Were it a salt it would, in all probability, be insoluble in benzene.

The Addition Products of p-Nitrosodimethylaniline with Diatomic Phenols.

These bodies divide themselves into two classes, those in which 1 molecule of the *p*-nitrosodimethylaniline unites with 1 molecule of the phenol, as was the case with trichlorresorcinol, and which reminds one of quinhydrone, which is made up of a molecule each of quinone and hydroquinone, and those in which the 2 molecules of the base unite with 1 molecule of the phenol, as was the case with tribromresorcinol and pyrocatechol.

Addition Product of p-Nitrosodimethylaniline and Trichlorresorcinol.

One gram of *p*-nitrosodimethylaniline, dissolved in benzene, was added to 1.5 grams of trichlorresorcinol in the same solvent. The product, which was also obtained by Edeleanu and Euescu, was purified by recrystallization from hot benzene, which gave a substance consisting of dark blue crystals, which, however, when ground up were reddish brown. Determination of chlorine:

0.2104 gram substance gave 0.2462 gram AgCl.

	Calculated for $ONC_6H_4N(CH_3)_2.C_6H_4Cl_3(OH)_2$.	Found.
Cl	29.27	28.94

This body dissolves in organic solvents, such as benzene, ether, chloroform, alcohol and acetone with a green color, and a molecular weight determination in benzene shows it to be an addition product which is practically completely dissociated on

solution. The molecular weight of the completely dissociated compound should be $\frac{363.5}{2}$ or 181.8.

Molecular Weight of Addition Product of p-Nitrosodimethylaniline and Trichlorresorcinol by the Ebullioscopic Method.

W.	s.	x.	K.	M.
100	0.5598	0.074	26.7	202
"	1.0757	0.145	"	198
"	1.6319	0.220	"	198
"	2.3078	0.311	"	198

Addition Products of p-Nitrosodimethylaniline and Tribromresorcinol.

The product obtained by mixing benzene solutions of tribromresorcinol and *p*-nitrosodimethylaniline differs from that from trichlorresorcinol in that it contains 2 molecules of the base to 1 of the phenol. The result is the same whether 1 molecule of the tribromresorcinol is mixed with 2 molecules of the aniline or with only 1 molecule. The product separates out in the form of light, olive-green crystals, which may be purified by crystallization from hot benzene. It melts at 115°.

The tribromresorcinol used in the preparation was analyzed and found to be pure.

The bromine determinations in the addition product gave the following results:

I. 0.1748 gram substance gave 0.1516 gram AgBr.

II. 0.1904 gram substance gave 0.1645 gram AgBr.

	Calculated for $[ONC_6H_4N(CH_3)_2]_2.C_6HBr_3(OH)_2$.	Found. I.	II.
Br	37.09	36.91	36.76

It is easily soluble in benzene, chloroform, acetone; also soluble in alcohol and ether; nearly insoluble in ligroin.

All of its solutions are *green*.

Addition Product of p-Nitrosodimethylaniline and Pyrocatechol.

Like tribromresorcinol, pyrocatechol gives a product in which 2 molecules of the base are united with 1 molecule of the phenol. Two grams of *p*-nitrosodimethylaniline, dissolved in 25 cc. of warm benzene, were added to 1.5 grams pyrocate-

chol in 50 cc. of benzene. An abundant yield of fine, olive-green crystals was obtained. The body, after recrystallization from hot benzene, melts, with decomposition, at 125°.

I. 0.3023 gram substance gave 36 cc. N at 18°.5 and 760.6 mm.

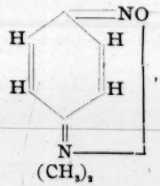
II. 0.3052 gram substance gave 37.9 cc. N at 23°.6 and 756.4 mm.

	Calculated for $[ONC_6H_4N(CH_3)_2]_2.C_6H_4(OH)_2$.	Found. I.	II.
N	13.66	13.73	13.88

The body is evidently an addition product composed of 2 molecules of the aniline and 1 of the phenol,

$$[ONC_6H_4N(CH_3)_2]_2.C_6H_4(OH)_2.$$

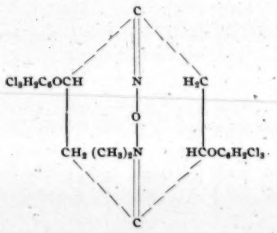
It dissolves in organic solvents with a green color. These addition products of *p*-nitrosodimethylaniline with mono- and diatomic phenols exhibit a rather striking analogy to the phenoquinone and quinhydrone, which have also been shown[1] to be addition products that completely dissociate in organic solvents. Paranitrosodimethylaniline is frequently given the quinone formula,



and inasmuch as Posner[2] has shown that in phenoquinone and similar compounds the point of addition of phenol is probably at the double bonds, and since this constitution is in harmony with the dissociation of these compounds, we are justified in suggesting that these addition products of *p*-nitrosodimethylaniline are of a similar nature. The analogy is further supported by the fact that *p*-nitrosodimethylaniline unites with 2

[1] THIS JOURNAL, 22, 167. Beltris Acad. Roy. d. Belgique, [iii], 32, 300; 33, 60.
[2] Ann. Chem. (Liebig), 336, 85.

molecules of a monatomic phenol, just as quinone does, whereas with a diatomic it unites with only 1 molecule (cf. quinhydrone), or 2 molecules of the aniline unite with 1 of the diatomic phenol. For example, the constitution of the addition product with trichlorphenol would be :



The constitution of the other addition product would be formulated in a similar manner.

Attempts to obtain corresponding compounds with pyrogallic acid and tetrachlorpyrocatechol were unsuccessful, instead of the addition products being readily soluble in organic solvents, dark brown or black substances were obtained, difficultly soluble and not giving in solution the characteristic bright green color of *p*-nitrosodimethylaniline.

The work described in this paper was done in the chemical laboratory of Radcliffe College.

VARIABLE SENSITIVENESS IN THE COLORIMETRY OF CHROMIUM.

By D. W. Horn.

It is either stated or implied in the descriptions of colorimetric methods that they are to be applied to dilute solutions.

This practice seems to have originated in the observation that the results of parallel determinations made in deeply colored (not very dilute) solutions do not approximate sufficiently to the average value. In some instances, as in the use of "Nessler's Reagent," there is a different color characterizing solutions that are recognized as too concentrated, but such instances are exceptional. In cases where alteration in concentration is not accompanied by any change in color, but only by a variation in the depth of the color, it has been, hitherto, merely a matter of individual judgment as to what shades are best adapted to the purposes of quantitative analysis.

The application of colorimetric methods in this general way involves one assumption at least, namely, that any given method is practically of equal sensitiveness in all solutions more dilute than those that are unmistakably too deeply colored for use. If, for convenience, we define as the sensitiveness of a colorimetric method the reciprocal of the weight in milligrams of the colored solute that produces that change in color that can just be differentiated with certainty, the assumption referred to is that the variations in the sensitiveness of any method are negligible.

Being about to make some colorimetric measurements, it occurred to me that this assumption was without experimental verification. It is evident that, if the sensitiveness of a colorimetric method should prove experimentally to be a variable, there must be for that method a set of definite conditions under which the sensitiveness will have a maximum value. Further, unless these conditions for maximum sensitiveness are determined experimentally for each of the colorimetric methods used for the accurate quantitative estimation of minute amounts of substances, the corresponding methods cannot be used with any assurance of maximum accuracy or with maximum ease in making the comparisons.

The results of an examination of the sensitiveness of the colorimetric estimation of chromium are presented in this paper. As similar results have been obtained by several observers in this laboratory, I am of the opinion that the effect of the personal equation on the general facts is negligible. The

results show that the sensitiveness is beyond a doubt variable, and that the *ease* of determination varies also with the concentration. The latter is measured, roughly, by the variation from the mean when the same two concentrations are compared without and with intermediate shades to aid in the comparison. The general relation between sensitiveness and concentration is not a simple one, nor such as would be likely to be predicted.

In the first column in the following table of results,[1] the concentrations at which comparisons were made are given in terms of the number of liters of solution containing 1 gram-atom of chromium; in the second, the weights of chromium in grams that could just be differentiated with certainty when present in 50 cc. of solution; in the third, the weights of potassium chromate in milligrams that could just be differentiated with certainty when present in 50 cc. of solution; in the fourth, the values for the sensitiveness; and in the fifth, the variation from the mean in grams of chromium shown by the values obtained when the comparisons were made with and without a number of solutions of concentrations and colors of nearly the same value, to aid in the differentiation from each other of the two most nearly alike:

I. Liters.	II. Grams.	III. Milligrams.	IV. Sensitiveness.	V. Grams.
250.0	0.003979	14.81	0.07	0.000500
500.0	0.000784	2.92	0.34	0.000048
666.6	0.000386	1.44	0.69	0.000050
1000.0	0.000184	0.69	1.45	0.000037
2000.0	0.000074	0.28	3.59	0.000000
3600.0	0.000007	0.03	33.33	
4000.0	0.000002	0.01	100.00	0.000000
7500.0	0.000003	0.01	100.00	
8000.0	0.000001	0.004	250.00	0.000000
9900.0	0.000005	0.02	50.00	
10666.6	0.000008	0.03	33.33	0.000001
16000.0	0.000011	0.04	25.00	0.000002
17700.0	0.000003	0.01	100.00	
32000.0	0.0000007	0.003	333.33	0.0000002
110000.0	0.000011	0.04	25.00	
150000.0	0.000008	0.03	33.33	
200000.0	not distinguishable from distilled water.			

[1] I am indebted to E. F. Bliss, M. D. Eby, A. I. Jonas, F. C. Child and A. Ross for many of the measurements made in connection with this subject.

In this case the sensitiveness had a maximum value at concentrations between 0.004 N and 0.008 N, with respect to the gram-atom of chromium. The ease with which the comparisons were made was also at a maximum at these concentrations, for complete agreement existed between the results obtained under the two sets of conditions already mentioned.

A rather anomalous fact appeared after the minimum amount of chromium that had to be present in the distilled water to give it a detectable color was determined. The minimum quantity required was 0.000013 gram of chromium, whereas 0.000001 gram produced a readily detectable difference in the depth of color at the concentrations of maximum sensitiveness. In other words, it was easier, by far, to tell the difference between two colored liquids than between a colored and a colorless one.

Some measurements of the sensitiveness of the colorimetry of chromium in solutions of green chromium chloride were also made. The results appear in the following table in columns corresponding to those in the previous table :

I. Liters.	II. Grams.	III. Milligrams.	IV. Sensitiveness.	V. Grams.
1000	0.000156	0.474	2.11	
1550	0.000084	0.255	3.92	
3000	0.000021	0.064	15.63	
9700	0.000268	0.815	1.23	

The decrease in sensitiveness at the last concentration given was probably due to precipitated chromium hydroxide resulting from the hydrolysis of the chloride. It is generally recognized that colorimetric comparisons cannot be made readily in turbid liquids. So far as determined, however, the general behavior of the sensitiveness is the same as in yellow chromium solutions.

Details of Experimental Work.

The comparisons were made in Nessler cylinders of 50 cc. capacity, with flat bottoms and of approximately the same internal diameter. The depth of colored liquid varied between 10 and 10.2 cm. Each cylinder was jacketed in black paper, such as is used in packing photographic plates. An efficient

form of stirring rod was used to insure uniformity in the liquids that were to be compared.

The solutions were measured from burettes of 50, 25, 10, or 2 cc. capacity, as best suited the volume that had to be measured. These, and the measuring flasks used, had been calibrated previously, though the corrections thus introduced proved, in the course of the work, to be negligible.

The comparisons were made in daylight reflected from a white porcelain surface, usually placed about a meter away from a north window. They were made at any hour of the day that was convenient, and on cloudy as well as on clear days.

The solutions were made from potassium bichromate that had been recrystallized 7 times from distilled water. Shortly before use it was fused in porcelain, broken up quickly in an agate mortar, and subsequently kept in a desiccator over concentrated sulphuric acid. Potassium hydroxide (Kahlbaum) was used in the solutions of the chromate in the proportion of 2 mol. to 1 of $K_2Cr_2O_7$. The green solutions were made by reducing the bichromate with alcohol and a small amount of hydrochloric acid; the greater part of the excess of alcohol and acid was driven off by evaporation on a water-bath before the solution was diluted.

The water used was the ordinary distilled water of the laboratory.

Two methods of comparison were employed, the one was that usually followed in colorimetric work—the method of approximation. When two concentrations were found that could not be distinguished from each other, a third was prepared slightly stronger than the stronger of the first two. When such a third solution was found that could be differentiated from the weakest, at least 5 times in 7 trials, the difference was recorded as just capable of being differentiated.

Several days later 2 solutions of concentrations that had previously been found to be just capable of differentiation were presented to the same observer. If the difference was not recognized another pair of tubes, differing somewhat more in concentration, was presented, and so on as long as necessary

for the establishment of a new limit for the difference in depth of color just distinguishable.

In all these cases the solutions were prepared and the tubes thoroughly mixed each time by some one who was not making the comparisons. The distinguishing marks on the cylinders were known only to this person, who also made a record of the result of each comparison, without telling the observer of the outcome of any one of them until all 7 had been made and recorded.

The other plan involved the preparation of a series of 7 or more solutions in which, beginning with the most dilute, there was a small but constant increment in the amount of colored solute present. When the members of this series included two that could be differentiated, it was comparatively easy to tell directly, by comparing several or all of them, just what difference in color was distinguishable and to just what amount of solute it corresponded. By selecting the concentrations properly and by having a sufficient number of tubes in the series, it was possible to arrive at the same result a number of times with different cylinders.

CHEMICAL LABORATORY,
BRYN MAWR COLLEGE,
November, 1905.

CINNAMYLIDENEACETIC ACID AND SOME OF ITS TRANSFORMATION PRODUCTS.

BY ARTHUR MICHAEL AND WIGHTMAN W. GARNER.

This work was originally taken up with a view to determine whether any evidence could be obtained bearing on the existence of more than two stereomeric forms in the homologues of cinnamic acid. δ-Phenyl-Δ^{α}-pentenoic acid,

$$C_6H_5CH_2CH_2CH : CHCOOH,$$

was selected for the purpose as being the substance most readily obtained, and it was proposed to carry out the investigation along the same lines that have been applied to the cinnamic acids. It has been shown that when β-allobromcinnamic acid (159°) is reduced with zinc dust and alcohol there is obtained,

in addition to allo- and cinnamic acids,[1] a lower melting product which, at the time this investigation was carried out, was regarded as a third isomeric acid.[2]

The cinnamylideneacetic acid was converted, by nascent hydrogen, into δ-phenyl-Δ^{β}-pentenoic acid and the latter transformed, by boiling with sodium hydroxide solution, into the Δ^{α}-acid. The dibromide of the Δ^{α}-pentenoic acid was then prepared by the addition of bromine, in chloroform solution. It was thought that a derivative of propiolic acid could be obtained from this dibromide by means of alcoholic potassium hydroxide, which, by the addition of hydrobromic acid, should give β-brom-Δ^{α}-phenylpentenoic acid. These changes may be represented by the following equations :

$$C_6H_5CH : CHCH : CHCOOH + H_2 = C_6H_5CH_2CH : CHCH_2COOH;$$

$$C_6H_5CH_2CH : CHCH_2COOH \rightarrow C_6H_5CH_2CH_2CH : CHCOOH;$$

$$C_6H_5CH_2CH_2CH : CHCOOH + Br_2 = C_6H_5CH_2CH_2CHBrCHBrCOOH;$$

$$C_6H_5CH_2CH_2CHBrCHBrCOOH - 2HBr = C_6H_5CH_2CH_2C : CCOOH;$$

$$C_6H_5CH_2CH_2C : CCOOH + HBr = C_6H_5CH_2CH_2CBr : CHCOOH.$$

However, on treating the Δ^{α}-pentenoic acid dibromide with alcoholic potassium hydroxide in excess, the original product, cinnamylideneacetic acid, was obtained and not a propiolic derivative. It appears, therefore, that the latter is unstable in the presence of alkali and, if formed at all, passes at once into the isomeric form :

$$C_6H_5CH_2CH_2C : CCOOH \rightarrow C_6H_5CH : CHCH : CHCOOH.$$

The question then arises, whether the rearrangement takes place with the removal of the first molecule of hydrobromic acid, or by the action of potassium hydroxide on the propiolic

[1] Liebermann : Ber. d. chem. Ges., **25**, 950.
[2] Michael and Whitehorn : *Ibid.*, **34**, 3647.

derivative? The problem is complicated by the fact that elimination of hydrobromic acid from the dibromide may occur in several different ways. Assuming that the β-bromine atom is first removed, the reaction may proceed in two directions:

$$C_6H_5CH_2CH_2CHBrCHBrCOOH \xrightarrow{HBr} \begin{cases} (1)\ C_6H_5CH_2CH_2CH : CBrCOOH \\ (2)\ C_6H_5CH_2CH : CHCHBrCOOH \end{cases}$$

Moreover, each of these acids can exist in two stereomeric forms. That a mixture of structurally different monobrom acids may be formed is indicated by the experiments of Fittig,[1] who showed that boiling β-monobrom derivatives of normal fatty acids with water leads to the formation of some Δ^{β}-acids, although in considerably less proportion than the Δ^{α}-derivatives. When the above acid dibromide is treated with alcoholic potassium hydroxide, in the proportion of 1 molecule of acid to 2 of the alkali, a product is obtained consisting of at least two isomeric monobrom acids. These acids do not appear to be stereomeric, for they are stable towards heat and can be esterified without change; if they should be stereomeric, at least they differ in their behavior from any similar acids as yet known.

A discussion of the changes that may occur when α-brom-Δ^{β}-phenylpentenoic acid (2) is boiled with alkali is more suggestive of possibilities than of probabilities, as, theoretically, the subject is exceedingly complicated and the experimental basis for such speculations is extremely limited.[2] Fittig[3] has, indeed, demonstrated that such Δ^{β}-alkenoic acids, whose γ-carbon is joined to alkyl or benzyl, when boiled with alkali are mainly converted into the Δ^{α}-isomers, but the process is never complete, as the latter acids go over, by addition of water, into the β-hydroxyalkanoic acids and these are partially converted into the original Δ^{β}-acids. If, however, phenyl replaces alkyl or benzyl, for instance with γ-phenyl-Δ^{β}-butenoic acid,

[1] Ann. Chem. (Liebig), 283, 61.

[2] The recent investigation of Riiber (Ber. d. chem. Ges., 38, 2742) shows how complicated the ultramolecular changes are in this series;

[3] Ann. Chem. (Liebig), 283, 61.

only traces of the acid undergo such a rearrangement. If an intramolecular rearrangement of unsaturation in the above monobrom acid precedes the elimination of hydrobromic acid, then, by analogy with the mother acid, the following change would take place :

$$C_6H_5CH_2CH : CHCHBrCOOH \rightarrow C_6H_5CH_2CH_2CH : CBrCOOH.$$

In order to obtain some experimental evidence on this point a number of aromatic acids were oxidized with potassium permanganate under different conditions. Those acids of the general type $C_6H_5CH : C(R)COOH$ invariably give benzaldehyde when oxidized in the presence of dilute sodium carbonate or strong potassium hydroxide. Phenylacetic acid gives benzaldehyde when dissolved in sodium carbonate, but does not give the aldehyde in the presence of much free alkali. Hydrocinnamic acid gives no aldehyde in either case. Δ^{α}-Phenylpentenoic acid, $C_6H_5CH_2CH_2CH : CHCOOH$, in the presence of free alkali, gives a small amount of benzaldehyde, but when the free acid is oxidized no aldehyde is obtained. The difference in conduct towards potassium permanganate between the last-mentioned acid and hydrocinnamic acid may, however, be due to the action of the alkali on the former, converting it, partially, into the Δ^{β}-acid, which gives the aldehyde on oxidation.

The mixture of monobrom acids obtained by the action of alcoholic potassium hydroxide on the phenyl-α,β-dibrompentenoic acid gives, on oxidation, in neutral solution, as well as when dissolved in sodium carbonate and in the presence of free alkali, small amounts of benzaldehyde. This fact seems to indicate that in the mixture of monobrom acids at least a part of the product has gone over into an acid whose unsaturated carbons are nearer to the phenyl than in a Δ^{α}-acid and that the formation of cinnamylideneacetic acid results without the previous formation of a propiolic derivative. Again, when the mixture of monobrom acids is boiled several hours, with a large excess of alcoholic potassium hydroxide, only a small yield of cinnamylideneacetic acid is obtained, not more than

10-20 per cent. By repeating the operation, a second quantity, approximately equal to the first, is obtained and, after the removal of this, the residue, consisting of the greater portion of the whole, still contains halogen. If this residue is esterified and the ester distilled *in vacuo*, hydrobromic acid is evolved and, after saponification with alcoholic potassium hydroxide, a small quantity of cinnamylideneacetic acid is again obtained. The residue, however, still contains bromine. It is evident, therefore, that the second atom of bromine is removed with very great difficulty from the dibromide, and further, that whatever the constitution of the intermediate products, the final result is always of the nature of an acrylic and not a propiolic derivative. This behavior appears to indicate a shifting of the position of the unsaturation before the elimination of hydrobromic acid occurs and that this rearrangement is in a reversible condition, as is the case in the experiments described by Fittig. This would explain why only a part of the monobrom acids is converted by each treatment with alkali. Although it cannot be said with certainty whether the rearrangement of the unsaturation takes place before or after the removal of the second bromine atom, the above results favor the former possibility.

Preparation of α,β-Dibrom-δ-phenylpentenoic Acid.

Cinnamylideneacetic acid, which forms the starting point in the preparation of the above-mentioned acid, was first made by Perkin, Sr.,[1] from cinnamic aldehyde and potassium acetate; later by Fittig and Mayer,[2] who modified the method of Perkin. Our material was obtained according to the directions of Fittig and Mayer, with some minor modifications. It was found that nearly all of the reaction product goes into solution when boiled with a large quantity of *dilute* sodium carbonate, whereas it is very difficultly soluble in strong alkali. A small amount of a tarry substance is dissolved along with the acid, but this can be removed by fractional precipitation with hydrochloric acid. The latter is carefully added until the precipitate begins to come down colorless and the solution is then fil-

[1] J. Chem. Soc., 31, 403.
[2] Ann. Chem. (Liebig), 268, 50.

tered. From the filtrate the acid can be precipitated in almost pure condition. The yield obtained is 30–35 per cent of the weight of the aldehyde used. This product was next reduced with sodium amalgam, according to the directions of Fittig and Hofmann,[1] and the resulting δ-phenyl-Δ^{β}-pentenoic acid boiled 10 hours with a 10 per cent aqueous solution of sodium hydroxide, containing 10 molecules of the latter to 1 of the acid.[2] After removal of the Δ^{α}-pentenoic acid, formed by the action of the alkali, by crystallization from ether, the mother liquor was again treated with sodium hydroxide and, finally, the process repeated a third time. The total yield obtained is about 60 per cent of the theoretical quantity.

Fittig and Perrin[3] prepared the dibromide of the Δ^{α}-pentenoic acid by addition of bromine to the acid dissolved in a mixture of ether and carbon bisulphide. By this method the halogen adds with difficulty, and much hydrobromic acid is formed in spite of all precautions. Better results were obtained in the following way: The acid is suspended in 15–20 volumes of dry chloroform, in a ground glass-stoppered bottle, the calculated quantity of bromine is then added and the mixture allowed to stand at a low temperature, 4 or 5 days, in diffused light. The addition product obtained in this way is recrystallized from a hot mixture of 2 parts benzene and 1 part ligroin, and shows the properties of Fittig and Perrins' dibromide.

Action of Alcoholic Potassium Hydroxide on α,β-Dibrom-δ-phenylpentanoic Acid.

To a solution of 20 grams of the dibromide in alcohol, somewhat more than the calculated quantity (2 mols.) of alcoholic potassium hydroxide was slowly added. After the mixture had been allowed to stand for several hours, the alcohol was evaporated on the water-bath, the residue dissolved in water, the solution extracted with ether and then acidified. The liberated acids, which were precipitated as a heavy oil, were

[1] Ann. Chem. (Liebig), 283, 309.

[2] Riiber (Ber. d. chem. Ges., 38, 2747) has recently shown that some Δ^{γ}-acid is also formed in this operation.

[3] Ann. Chem. (Liebig), 283, 326.

taken up with ether. After removal of the latter the residue was dissolved in hot chloroform and 2 volumes of ligroin added to the solution. On standing, clusters of fine needles separated which melted at 67°–75° and were soluble in all ordinary media except ligroin. There were obtained 6 grams of this product. Repeated recrystallization from a mixture of chloroform and ligroin did not improve its melting point, which likewise remained unchanged after repeated fusion of the acid mixture. Analysis:

0.1542 gram substance gave 0.1151 gram AgBr.

	Calculated for $C_6H_5C_2H_3C_2HBrCOOH$.	Found.
Br	31.37	31.73

By spontaneous evaporation of the mother liquors a heavy oil, easily soluble in all the common organic solvents except ligroin, was precipitated. This oil contained bromine but could not be obtained in a solid form. A second portion of the dibromide was boiled 4 hours with an equal weight of potassium hydroxide dissolved in alcohol. A thick oil was obtained which contained bromine, but did not solidify on long standing. The treatment with alcoholic potassium hydroxide was variously modified as to time of boiling and quantity of alkali used, but all efforts to obtain a crystalline product in this way were unsuccessful.

An attempt was made to obtain better results through the ester dibromide. Twenty grams of the Δ^{β}-acid were esterified by treatment with sulphuric acid and alcohol, according to the Purdie method.[1] The ester was obtained as an oil boiling at 178° (25 mm.). This was dissolved in 2 volumes of carbon bisulphide and the calculated quantity (1 mol.) of bromine, in carbon bisulphide, slowly added. Addition took place very readily and without the formation of more than traces of hydrobromic acid. The ester dibromide was then treated with 2 molecules of alcoholic potassium hydroxide in the cold, but as the resulting product could not be brought to crystallize it was converted into the ethyl ester, which boiled at 178°–184° (8–11 mm.) but with so considerable a decomposition that it was

[1] J. Chem. Soc., 39, 346.

not considered sufficiently pure for further experiments. Finally, 20 grams of the acid dibromide were converted into the mixture of monobrom acids by treatment with cold alcoholic potassium hydroxide, the product converted into the ethyl ester and this boiled 6 hours with 0.6 of its weight of potassium hydroxide, dissolved in 5 parts of alcohol. A thick oil was obtained which contained halogen. This was dissolved in hot, 60 per cent alcohol and, on standing, about 2 grams of a crystalline substance separated out which melted at 165° and showed the other properties of cinnamylideneacetic acid. The oil from the mother liquor was again treated with alcoholic potassium hydroxide in the same manner and about the same quantity of cinnamylideneacetic acid was again obtained. The residual oil, which still showed the presence of bromine, was esterified and the resulting ester distilled in a vacuum. In the first distillation a heavy oil went over at 180°–195° (18 mm.) with evolution of much hydrobromic acid. This was again distilled and boiled at 180°–185° (18 mm.). After saponifying with alcoholic potassium hydroxide and crystallizing from benzene, cinnamylideneacetic acid was once more obtained. Similar results were also observed by treating the dibromide directly with a large excess of alcoholic potassium hydroxide.

Oxidation of Some Aromatic Acids.

A dilute solution of potassium permanganate was allowed to drop slowly into a boiling solution of the acid to be oxidized and the resulting distillate examined for aldehyde. A simple and convenient form of apparatus for conducting the experiment consists of a distilling flask, the neck of which is fitted with a dropping funnel and the side tube connected with a condenser. Under these conditions the aldehyde formed in the first stages of the oxidation passes over at once, in part at least, and thus escapes the further action of the permanganate. The aldehydes were identified by precipitation as phenylhydrazones or as semicarbazones. Each of the acids examined was oxidized with the permanganate under different conditions, as follows: (1) In the free state; (2) dissolved in sodium carbonate; (3) in the presence of a large excess of free alkali.

Each of the acids of the cinnamic acid type was found to give benzaldehyde under all the above-mentioned conditions. The acids belonging to this group, which were examined, are cinnamic acid, α-bromcinnamic acid, α-ethylcinnamic acid and α-butylcinnamic acid. Phenylacetic acid, in dilute sodium carbonate solution, gives benzaldehyde, but in the presence of free alkali does not give the aldehyde. This behavior affords a means of detecting the cinnamic acid derivatives in the presence of phenylacetic acid.

Hydrocinnamic acid gives no aldehyde in sodium carbonate solution, which fact differentiates it from the cinnamic acid group; nor does it give any aldehyde in the presence of free alkali, in which respect it differs from phenylacetic acid. δ-Phenyl-Δ^{α}-pentenoic acid, $C_6H_5CH_2CH_2CH : CHCOOH$, gives benzaldehyde in the presence of free alkali, but when the free acid is oxidized no aldehyde is obtained.

The mixture of monobrom acids resulting from the action of alcoholic potash on the dibromide,

$$C_6H_5CH_2CH_2CHBrCHBrCOOH,$$

gives benzaldehyde when oxidized in the free state, as well as in the presence of carbonate and free alkali. The identity of the aldehyde was established by converting it into the phenylhydrazone, m. p. 152°, and also into the semicarbazone, m. p. 214°.

Hydrocinnamic Aldehyde.

Since the formation of this aldehyde was not excluded in some of the experiments described above, it was prepared according to directions of v. Miller and Rohde.[1] Hydrocinnamic aldehyde reacts with semicarbazine hydrochloride to form a semicarbazone, which crystallizes in colorless leaflets, easily soluble in alcohol, but difficultly soluble in water. It melts at 125°. Analysis:

0.1133 gram substance gave 21.7 cc. N at 21° and 767 mm.

[1] Ber. d. chem. Ges., 23, 1080.

	Calculated for $C_6H_5C_2H_4CHCH_3ON_2$.	Found.
N	21.98	22.02

TUFTS COLLEGE, MASS.

MAGNESIUM PERMANGANATE AS AN OXIDIZING AGENT.

BY ARTHUR MICHAEL AND WIGHTMAN W. GARNER.

The use of potassium permanganate, in aqueous solution, carries with it the formation of a strong alkali, which may act in an undesired manner on the substance to be oxidized, or on the products formed in the oxidation. To obviate this difficulty it has been suggested to carry out the process in the presence of a current of carbon dioxide; or, to add magnesium chloride to the oxidizing mixture and in this way render the caustic alkali inert, inasmuch as it should at once react with the chloride and form the comparatively inactive magnesium hydroxide.[1] A simpler way would be to employ magnesium permanganate as the oxidizer; moreover, the decided tendency of magnesium salts to pass over into magnesium hydroxide when heated with water, seemed to indicate that this salt should possess an unusual capacity for oxidation.

Magnesium permanganate was first prepared by Mitscherlich[2] and later examined in his laboratory by Aschoff.[3] They obtained the salt by treating an aqueous solution of barium permanganate with magnesium sulphate, or the corresponding silver salt with magnesium chloride, and describe it as a deliquescent, crystalline substance, with 6 molecules of water of crystallization. Recently it has been prepared by Chambliss,[4] by treatment of permanganic acid with magnesium hydroxide; he found that when heated on a water-bath, in aqueous solution, it is rapidly decomposed, giving off oxygen and ozone, and he also called attention to the strong oxidizing power of such a solution.

We first prepared the salt by treating silver permanganate,

[1] Lossen: Ann. Chem. (Liebig), 201, 370.
[2] Gmelin-Kraut: Anorg. Chem., II³, p. 527.
[3] *Ibid.*
[4] Dissertation, Johns Hopkins University (1900).

suspended in hot water, with an equivalent quantity of magnesium chloride. The first method of Mitscherlich, however, gave better results. Barium permanganate[1] was prepared from the potassium salt, according to the method of Muthmann,[2] the aqueous solution of the barium salt thus obtained was standardized by means of oxalic acid, and the barium precipitated by the addition of the necessary quantity of magnesium sulphate. The filtrate from the barium sulphate was evaporated on the water-bath to dryness. The product thus obtained has a crystalline structure and bluish-gray metallic luster. In order to completely desiccate the salt it was heated at 100°, in a vacuum, for several days and it appeared to undergo but little decomposition by this treatment. Its metallic luster was not wholly lost, though its color changed from blue to a purplish tint, resembling that of the potassium salt.[3]

We found anhydrous magnesium permanganate to be insoluble in chloroform, carbon tetrachloride, benzene, toluene, nitrobenzene, ligroin, ether and carbon bisulphide and without action on these compounds at ordinary temperatures, unless some solvent was added to bring about solution of the salt. Methyl alcohol dissolves it in considerable quantity, forming a solution which is tolerably stable at ordinary temperatures, while ethyl and propyl alcohols are attacked instantly. The methyl and ethyl esters of acetic acid dissolve the salt to some extent and form comparatively stable solutions. It also dissolves quite readily in glacial acetic acid and the solution remains unchanged after several hours at room temperature. Propionic acid is attacked more readily, while butyric and isovaleric acids are decomposed with violence and with evolution of carbon dioxide. Acetone dissolves the salt, but is at once attacked with considerable evolution of heat. By way of comparison, it may be mentioned that Peau de Saint-Gilles[4] found that potassium permanganate is fairly soluble in acetone and

[1] This salt is now a commercial product.

[2] Ber. d. chem. Ges., 26, 1016.

[3] A sealed tube containing some of the salt exploded during the summer, although it was kept in diffused light.

[4] Ann. Chim. Phys., [3], 55, 396. Sachs: Ber. d. chem. Ges., 34, 497. Such a solution has been employed as an oxidizing mixture, *vide* Sachs: Ber. d. chem. Ges., 34, 497. Michael and Leighton: J. prakt. Chem., 68, 523.

the solution is quite stable even when boiled. Other aliphatic ketones, which are oxidized with difficulty by potassium permanganate, are at once attacked by the magnesium salt; lactic and other hydroxy acids, as well as keto acids, are also immediately destroyed. Of all the solvents examined, only two were found to be sufficiently stable toward the salt to be of any practical use for oxidation purposes, *viz.*, glacial acetic acid and pyridine.

Dissolved in glacial acetic acid, magnesium permanganate is an extremely powerful oxidizing agent. When such a solution is added to benzene, surrounded with a mixture of salt and ice, a constant current of carbon dioxide is evolved. This is a striking fact when the extraordinary stability of benzene toward other oxidizing agents is taken into consideration. Carius[1] oxidized benzene with a mixture of manganese dioxide and sulphuric acid and succeeded in isolating, besides carbon dioxide, formic, benzoic and phthalic acids as products of the oxidation, but these organic acids are all instantly destroyed in the cold by magnesium permanganate in acetic acid solution, and we were unable to separate an intermediate product in the oxidation of benzene to carbon dioxide.

The homologues of benzene show the same conduct towards the solution of the salt as does benzene itself. Moreover, open-chain hydrocarbons, such as hexane, which are also extremely stable towards the usual oxidizing agents, are likewise readily decomposed, yielding carbon dioxide.

Potassium permanganate is almost insoluble in glacial acetic acid, but is fairly soluble in acetic anhydride,[2] forming a solution which is only slowly oxidized on standing. Such a solution is, however, not to be compared with that of the magnesium salt in glacial acetic acid as regards its oxidizing power. Benzene, toluene and hexane are scarcely attacked in the cold, and even ketones are only oxidized with difficulty.

Magnesium permanganate dissolves more easily in pyridine

[1] Ann. d. Chem., 148, 50. Carius used a mixture of 5 parts sulphuric acid to 1 of water, which dissolved some of the benzene. Although he states that no chemical action takes place when the hydrocarbon dissolves, he does not appear to have examined whether a slow chemical action does not occur.

[2] It is considerably more soluble in the anhydride than in acetone.

than in glacial acetic acid, but the solution in the former solvent has surprisingly weak oxidizing powers. In fact, those compounds, such as alcohol, acetone and ethyl acetate, which are in themselves solvents for the salt, are acted on less readily in the presence of pyridine than when used alone, that is, pyridine seems to exert an inhibitory influence on the salt as an oxidizer. A solution of the permanganate in a mixture of acetic acid and pyridine is not stable, although either solvent, taken alone, forms a stable solution. Potassium permanganate is also readily soluble in pyridine but, as in the case of the magnesium salt, the solution shows very weak oxidizing powers. Methyl alcohol is more slowly attacked than when treated with the salt alone; acetone is stable as is also ethyl acetate, while ethyl alcohol is oxidized fairly readily. Quinoline dissolves the magnesium salt, but the solution is unstable and this base is also slowly attacked in the presence of pyridine.

From the above-mentioned experiments it appears that anhydrous magnesium permanganate, in some solvents, completely destroys the benzene ring, while pyridine is attacked with very great difficulty. In the aliphatic series the higher hydrocarbons and their derivatives are oxidized very readily to carbon dioxide, whereas the lower members, particularly in the first two carbon series, are comparatively stable. The importance of the nature of the solvent used is strikingly shown in the cases of glacial acetic acid and pyridine. Not only is the pyridine solution surprisingly stable, but the inhibitory effect of the base in preventing otherwise easy oxidations is difficult to understand, especially as there is no evidence of a chemical union between it and the salt.

These preliminary experiments are suggestive along several lines. It would be interesting to ascertain whether magnesium permanganate, in aqueous solution, would show itself so destructive to aromatic substances as it does in acetic acid. That the aqueous solution will prove of use in case of difficultly oxidizable substances and in oxidations where it is desirable to prevent the formation of an alkaline solution, seems

very probable.[1] Again, if substitution products of pyridine are also stable towards the acetic acid solution, the mixture will undoubtedly be of service in the degradation of the many complicated derivatives of the base. The solution of potassium permanganate, in acetic anhydride, may also prove valuable in certain oxidations, as acetic anhydride is not only a ready solvent for many substances that are difficultly soluble in water, but it acts readily on substances containing a hydroxyl or formyl group, to form products that may be less susceptible to oxidation, and the anhydride may, in this way, to a certain extent, protect the intermediary products of oxidation and enable their isolation.

TUFTS COLLEGE, MASS.

ON SOME CUPRAMMONIUM SALTS.

BY D. W. HORN.

The object of this paper[2] is to call attention to some cuprammonium oxalates that I have obtained and to their bearing on the question of *types* in this class of salts.

The compositions of the oxalates correspond to the empirical formulæ :

$$CuC_2O_4.5NH_3;$$
$$CuC_2O_4.4NH_3.2H_2O;$$
$$CuC_2O_4.2NH_3;$$
$$CuC_2O_4.2NH_3.2H_2O;$$
$$CuC_2O_4.NH_3.$$

Only the fourth of these has been described previously.

The preparation of the oxalates is a part of a study of those cuprammonium salts that can be obtained from aqueous solutions, with a view to determining whether there is any effect of the acid residue upon the composition or stability of the salt, or of its complex ion.

[1] According to Ullmann and Uzbachian (Ber. d. chem. Ges., 36, 1797) the calcium salt does not seem to be a more powerful reagent than potassium permanganate.

[2] This paper was read, in part, before the Philadelphia Section of the American Chemical Society, Sept. 21, 1905.

The question of this effect is raised by the differences in physical properties of some cuprammonium salts. It has been shown that the effect of the addition of 4 molecules of ammonia to 1 molecule of copper sulphate, dissolved in water, is to increase the molecular lowering by 7°.7 and the equivalent conductivity by 16.6 reciprocal ohms, whereas a similar addition to copper nitrate, at comparable dilutions, increases the molecular lowering 2°.5 and the equivalent conductivity by 6.9 reciprocal ohms.[1] In the case of copper nitrate, additions of ammonia in excess of 4 molecules to every molecule of dissolved nitrate give normal values for the ratio between the changes in viscosity and in concentration, whereas, under similar circumstances, with copper sulphate the values for this ratio are higher than the normal values.[2] Cupritetrammonium nitrate can be recrystallized from water ;[3] cupritetrammonium sulphate is decomposed rapidly by water.[4] Cupritetrammonium chloride cannot be distinguished from the corresponding sulphate, when the salts are studied as to their effect on the ratio of distribution of ammonia between their aqueous solutions and chloroform.[5] Cupritetrammonium tartrate is stable in the air and stable in its solutions for a very long time ;[6] the corresponding sulphate decomposes rapidly in the air, and its aqueous solutions deposit basic salts within a day or two.[7] The formulæ of these salts are :

$$CuSO_4.4NH_3.H_2O\ ;^{8}$$
$$CuCl_2.4NH_3.H_2O\ ;^{9}$$
$$Cu(NO_3)_2.4NH_3\ ;^{10}$$
$$CuC_4H_4O_6.4NH_3.^{11}$$

[1] Reychler : Ber. d. chem. Ges., **28**, 555 (1895).
[2] Blanchard : J. Am. Chem. Soc., **26**, 1315 (1904).
[3] Kane : J. prakt. Chem., **15**, 276 (1838). Ann. Chim. Phys., [2], **72**, 225, 265, 337 (1838).
[4] Horn and Taylor : THIS JOURNAL, **32**, 253 (1904). Sabbatani : Jahres. d. Chem. 1891, pp. 1. 777.
[5] Dawson and McCrae : J. Chem. Soc., **79**, 1072 (1901).
[6] Schiff : Ann. Chem. (Liebig), **123**, 46 (1862).
[7] Horn and Taylor ; *Loc. cit.*
[8] Berzelius : Ann. d. Phys. (Gilbert), **40**, 300 (1813).
[9] Kane : *Loc. cit.*
[10] Kane : *Loc. cit.* I have confirmed these formulæ.
[11] Schiff : *Loc. cit.*

These suggest, as a possible explanation of the difference in behavior, *either* the effect of the "water of crystallization," or the effect of the different acid residues. The matter may be approached experimentally by preparing cuprammonium salts of the several acids under corresponding conditions and comparing them.

I. Dihydrated Cupridiammonium Oxalate.

This is one of the longest known among cuprammonium salts. Vogel[1] obtained it accidentally while trying to make a double oxalate of copper and ammonium. Seubert and Rauter[2] corrected Vogel's analytical errors and established for the salt the formula

$$CuC_2O_4.2NH_3.2H_2O,$$

in the place of the one Vogel had assigned, *viz.*:

$$CuC_2O_4.2NH_3.H_2O.$$

Preparation.—This salt results when the solution, obtained by treating strong ammonia water with just as much copper oxalate as it can dissolve in the cold, is exposed in an evaporating dish to the air for several hours (Vogel); when a solution of copper oxalate in an excess of ammonia is allowed to evaporate in the air; or when a solution of copper oxalate in concentrated ammonia is diluted cautiously with water (Seubert and Rauter); when a solution of cupritetrammonium sulphate is treated with an equivalent solution of potassium oxalate, in the presence of an excess of ammonia (Kohlschutter).[3] Unless precautions are taken, the solution may be heated through 30° or more by the heat evolved as the oxalate dissolves in the ammonia water; so long as the resulting solution is unsaturated with respect to copper oxalate, the same salt separates out when the solution is cooled suddenly as when it cools gradually.

The specimen used in the first two of the following analyses was prepared by the gradual cooling of an unsaturated solution

[1] J. f. Chem. Phys. (Schweigger), **7**, 1 (1813).
[2] Ber. d. chem. Ges., **25**, 2821 (1892).
[3] *Ibid.*, **37**, 1153 (1904).

of copper oxalate in dilute ammonia water, and for the last two analyses the specimen was prepared by rapid cooling of a similar solution.

Weight of salt taken for analysis. Gram.	Volume of acid neutralized by ammonia. cc.	Percentage of ammonia found.	Percentage calculated for $CuC_2O_4.2NH_3.2H_2O$.
0.3311	14.04	15.42	15.40
0.3478	14.92	15.26	
0.1862	7.94	15.51	
0.2796	13.32	15.20	

Characteristics.—Large, brilliant crystals of this salt form very readily. Vogel described these as short pieces of six-sided, much flattened columns, with two broad sides opposite each other and with four small faces. Seubert and Rauter describe them as "triclinic." A large number of these have been examined with the polarizing microscope and it has been found that they invariably show parallel extinction and the biaxial brush in convergent light; the crystals, therefore, are orthorhombic. The axis of greatest elasticity is parallel to the longest direction of the crystal; that is, presumably, $\mathfrak{C} = \dot{C}$.[1] The crystals effloresce in the air, due to the loss of both ammonia and water. In a desiccator over lime and potassium hydroxide they effloresce so slowly that they may be dried in this way for analysis. If the salt is heated it decomposes gradually at first, but the decomposition soon becomes violent and the specimen that is being heated is scattered. Such a result cannot be avoided even by very cautious heating in hydrogen. The salt has a blue color, quite like that of the crystallized copper nitrate, $Cu(NO_3)_2.3H_2O$. Its color could not possibly be confused with the deep purple-blue of the tetrammonium salts like cupritetrammonium sulphate.

II. Anhydrous Cupridiammonium Oxalate.

Preparation.—This compound is formed while a hot, saturated solution of copper oxalate in ammonia water, sp. gr. 0.9, is cooling. A convenient way to obtain it is to filter the hot solution, for the salt separates from the solution with great

[1] I am indebted to Dr. F. Bascom for the examination of the crystals described in this paper.

rapidity and most of it will be found upon the filter. Analysis of an air-dried specimen:

Weight of salt taken.	Volume of acid neutralized by the ammonia.	Percentage of ammonia found.	Percentage calculated for $CuC_2O_4.2NH_3$.
Gram.	cc.		
0.1748	9.10	18.94	18.38
0.2877	14.64	18.51	

Weight of salt taken.	Weight of cuprous sulphide obtained.	Percentage of copper found.	Percentage calculated for $CuC_2O_4.2NH_3$.
Gram.	Gram.		
0.1833	0.0775	33.77	34.24
0.2192	0.0924	33.66	

Some of this same salt may separate from a saturated solution of copper oxalate in ammonia, made for the purpose of preparing the dihydrated salt. In such cases the anhydrous salt always separates first. The following are single analyses of specimens of the anhydrous salt obtained from such solutions:

Weight of salt taken.	Weight of cuprous sulphide obtained.	Percentage of copper found.	Percentage calculated for $CuC_2O_4.2NH_3$.
Gram.	Gram.		
0.0509	0.0217	34.04	34.24
0.2410	0.1022	33.87	

Characteristics.—This salt separates as a sandy powder, which consists of very small crystals that are highly doubly-refracting. They are orthorhombic and the axis of least elasticity is parallel to the longest direction of the crystal; that is, presumably, $\breve{C} = \dot{C}$. The salt is fairly stable in the air and can be dried for analysis between filter papers. The phenomena that accompany its decomposition by heat are the same, in general, as those accompanying the decomposition of the dihydrated salt, except that the decomposition becomes more violent. The salt exhibits an unusually intense blue color that is very striking and by which it could be distinguished from any other blue salt that I know of.

Vogel probably prepared this salt, but on account of faulty analyses ascribed to it an erroneous formula, *i. e.*, $CuC_2O_4.NH_3$.

This formula appears in some of the reference books.[1] In his paper Vogel states that "if one introduces into a vessel of ammonia water more copper oxalate than the ammonia can dissolve, the copper oxalate on the bottom of the vessel changes into a pulverulent, sandy mass, which is very similar to strongly-colored, dark blue smalt, its color having a great deal of brilliancy (Feuer). From the supernatant mother liquor the efflorescent salt $CuC_2O_4.2NH_3.2H_2O$ crystallizes subsequently, and then the mother liquor is colored feebly green." It is impossible to draw any conclusion from the results of his analysis; for example, the percentage of copper oxide found by him lies almost exactly half way between the percentage required by the formulæ $CuC_2O_4.2NH_3$ and $CuC_2O_4.NH_3$. His description of the physical properties of the substance agrees very closely with the properties of the salt $CuC_2O_4.2NH_3$, and the additional fact that the supernatant liquid subsequently yielded the dihydrated salt is entire agreement with the assumption that Vogel had the anhydrous diammonium oxalate. Seubert and Rauter make no reference to this anhydrous diammonium salt, nor to Vogel's description of it. I attempted to reproduce the conditions stated by Vogel; to this end, copper oxalate was ground in a porcelain mortar for more than half an hour with ammonia water, sp. gr. 0.9. After it had been dried over potassium hydroxide, the material thus obtained was analyzed for ammonia. The percentages found were 17.01 and 17.99, values that approach the 18.38 required by the formula $CuC_2O_4.2NH_3$. This point is of especial interest because I have obtained a salt of composition represented by the formula $CuC_2O_4.NH_3$, the formula that Vogel erroneously assigned to the intensely blue salt, $CuC_2O_4.2NH_3$. As will be seen in the next paragraph, the salt that actually has the formula $CuC_2O_4.NH_3$ differs very much in its properties and preparation from the salt to which Vogel had assigned this same formula.

III. Cuprimonammonium Oxalate.

Preparation.—After the mother liquor has completely de-

[1] Handb. d. Org. Chem., Beilstein, 2 ed., I., p. 582. Handwörterb. d. Chem., Ladenburg, VIII., p. 405.

posited the two salts already described, $CuC_2O_4.2NH_3$ and $CuC_2O_4.2NH_3.2H_2O$, the residual solution is colored feebly green, as stated by Vogel. If this green liquid is allowed to stand exposed to the air for some time, small crystals of the salt $CuC_2O_4.NH_3$ are formed. These are firmly attached to the walls of the crystallizing dish containing the liquor. The amount of oxalate deposited in this form is relatively small. The following are the results of the analysis of this salt:

Weight of salt taken.	Weight of cuprous sulphide obtained.	Percentage of copper found.	Percentage calculated for $CuC_2O_4.NH_3$.
Gram.	Gram.		
0.2094	0.0981	37.40	37.71
0.1741	0.0817	37.50	

Weight of salt taken.	Volume of acid neutralized by ammonia.	Percentage of ammonia found.	Percentage calculated for $CuC_2O_4.NH_3$.
Gram.	cc.		
0.1569	4.43	10.27	10.37
0.1671	4.86	10.34	

Characteristics.—This salt separates in the form of hard, brilliant, very small crystals. When examined with the polarizing microscope they proved to be orthorhombic and of prismatic habit. The axis of greatest elasticity is parallel to the longest direction of the crystal; that is, presumably, $\mathfrak{C} = \dot{c}$. The color of the crystals is pale green. When heated, the salt decomposes with violence and leaves a deposit resembling amorphous carbon.

IV. Dihydrated Cupritetrammonium Oxalate.

Preparation.—When a solution of copper oxalate in ammonia water is saturated with ammonia gas, this salt separates out as the concentration of the ammonia in the solution increases. If the original solution is made by taking more than 5 volumes of water to 1 of ammonia water, sp. gr. 0.9, the yield of the salt becomes very small and it is usually necessary to chill the solution in ice-water to obtain any considerable amount of it. In strong solutions the salt may begin to crystallize at temperatures as high as 35°. Analysis:

Weight of salt taken.	Weight of cuprous sulphide obtained.	Percentage of copper found.	Percentage calculated for $CuC_2O_4.4NH_3.2H_2O$.
Gram.	Gram.		
0.3649	0.1124	24.60	24.85
0.4402	0.1358	24.63	
0.4337	0.1339	24.65	

Weight of salt taken.	Volume of acid neutralized by ammonia.	Percentage of ammonia found.	Percentage calculated for $CuC_2O_4.4NH_3.2H_2O$.
Gram.	cc.		
0.5131	37.63	26.69	26.67
0.5786	42.44	26.69	

Characteristics.—This salt separates from warm, concentrated solutions in crystals that are 2–3 mm. in greatest length. If a mother liquor that is yielding the salt is filtered and evaporated at ordinary temperatures, in a desiccator, over lime, crystal masses as much as 4 cm. in length may be obtained. These crystals cannot be examined except through the glass cover of the desiccator, but, apparently, they are monoclinic, showing orthodome and basal pinacoid and ortho- and clino-pinacoids developed in the prismatic zone. The salt is extremely unstable when separated from its mother liquor. It cannot be dried, at ordinary temperatures, with any degree of assurance that decomposition will not set in. It can be dried, however, over lime, in a desiccator kept at about 5°, in an ice-chest. When exposed to the air, even the dry salt decomposes with great rapidity. Its instability was clearly shown in one case, where a glass stoppered weighing tube containing some of the salt was shaken rather violently to break up some lumps of crystals prior to weighing for analysis; the stopper was blown repeatedly from the tube by the ammonia evolved in the rapid decomposition that followed this disturbance. When the decomposition has once been started by any cause, it appears to advance under the conditions in which the salt had previously seemed to be stable. Unlike any of the oxalates previously mentioned, this salt readily parts with its ammonia when it is cautiously heated in hydrogen; under these circumstances the decomposition does not take place with any violence. If heated in the air, however, the decomposition becomes violent.

The color of the salt is deep purple-blue, closely resembling that of cupritetrammonium sulphate.

Kohlschutter in his work realized conditions under which this or some other tetrammonium oxalate was to be expected. He treated cupritetrammonium oxalate, in solution, with an equivalent solution of potassium oxalate, in the presence of an excess of ammonia. The product, however, was the dihydrated diammonium salt. He thinks this result is "clearly to be ascribed to the tendency of the oxalic acid residue to enter into direct union with the copper atom, ... a tendency that displays itself in the instantaneous combination of the cupric ion with the oxalic acid ion to form the completely insoluble copper oxalate."[1] If such a tendency can be fairly assumed, it is obvious that it has a limit and vanishes under proper conditions.

V. Cupripentammonium Oxalate.

Preparation.—This salt was obtained when a hot, saturated solution of copper oxalate in ammonia water, sp. gr. 0.9, was saturated with ammonia gas as it cooled. Analysis:

Weight of salt taken. Gram.	Weight of cuprous sulphide obtained. Gram.	Percentage of copper found.	Percentage calculated for $CuC_2O_4.5NH_3$.
0.3466	0.1155	26.62	26.84
0.3797	0.1269	26.69	
0.4343	0.1455	26.75	

Weight of salt taken. Gram.	Volume of acid neutralized by ammonia. cc.	Percentage of ammonia found.	Percentage calculated for $CuC_2O_4.5NH_3$.
0.3340	32.15	35.02	36.01
0.4466	43.15	35.15	
0.3328	32.62	35.66	

Characteristics.—This salt appears in crystals closely resembling those of the tetrammonium oxalate, but slightly more purple in color. Its instability is very great. Like the tetrammonium salt, it is readily deprived of its ammonia when it is cautiously heated in an atmosphere of hydrogen. When its

[1] Kohlschutter: *Loc. cit.*

solution in warm ammonia water, sp. gr. 0.9, is cooled, the tetrammonium oxalate crystallizes out.

Of these oxalates, the monammonium and pentammonium salts contain copper and ammonia in ratios in which they have never before been observed in salts prepared from *solution*. Two sulphates of corresponding formulæ have been described, but both of these salts have been made only by the action of dry ammonia on anhydrous copper sulphate.

The pentammonium salt *obtained from aqueous solutions* raises the question of the existence of an ion $\overset{+}{Cu}(\overset{+}{NH_3})_5$. As is obvious from the formulæ and from the method of preparation, the case of the oxalates is not analogous to that of the sulphates

$$CuSO_4.5NH_3,$$
$$CuSO_4.4NH_3.H_2O,$$
$$CuSO_4.4H_2O.H_2O,$$

from the point of view emphasized by Werner. He represents the one cuprammonium sulphate as $Cu(NH_3)_4.SO_4.H_2O$,[1] which should yield the kathion $Cu(\overset{++}{NH_3})_4$; the other cuprammonium sulphate is not assigned a structural formula, but this class of salts is dismissed with the statement that "the number of compounds with the complex (MA_5) is too small to be discussed here at present."[2] The pentahydrate, however, is represented as $Cu(H_2O)_4SO_4.H_2O$.[1]

The most obvious assumption is that there is an ion $Cu(\overset{++}{NH_3})_6$. The existence of this ion has already been assumed by Locke,[3] who, in interpreting the values he had found for the "combined ammonia," in ammoniacal solutions of copper sulphate, estimated that about 3 per cent of the total copper must be present in a higher complex, $Cu(\overset{++}{NH_3})_5$ or $Cu(\overset{++}{NH_3})_6$, when the concentration of copper is 0.1175 molar and that of ammonia normal.

[1] Z. anorg. Chem., 3, 309 (1893).
[2] *Ibid.*, 2, 303.
[3] This Journal, 31, 268 (1904).

These 5 oxalates do not fit in with the two generally accepted types of cuprammonium compounds that Kohlschutter says are now recognized in most text-books and books of reference. The types are $Cu(NH_3)_4X_2$ and $Cu(NH_3)_2X_2$; they are to be regarded as *fundamental* types because "by far the larger number of cuprammonium salts contain 2 or 4 ammonia groups in the molecule." There is, however, no apparent reason why any one of these 5 oxalates should be assumed to be of a more fundamental type than any other one. It is true that some of them contain copper and ammonia in ratios that are not common, but at present this can as well be regarded as due to the comparatively undeveloped condition of the chemistry of cuprammonium salts as to any assumed peculiarity in copper and ammonia that would cause them to combine more frequently in the ratios 1 : 4 and 1 : 2 than in other ratios.

Any conception of one type as more "fundamental" than any other can be drawn only from comparisons of the formulæ of the cuprammonium salts that are to be found in the records, but it is imperative that only comparable cases should enter as data in such comparisons. Cuprammonium salts that have been separated from solutions containing other salts, or from solutions to which alcohol has been added, cannot, at present, be compared with cuprammonium salts that have separated from solutions containing only the copper salt, ammonia and water. Kohlschutter's work[1] shows that the presence of other salts affects the complexity of the cuprammonium salt that subsequently separates from the same solution, and Dawson and McCrae[2] have called attention to the probable disturbing influence of alcohol on the equilibrium between copper and ammonia.

The simple cuprammonium salts that have so far been obtained from aqueous solutions, in the absence of other electrolytes and in the absence of alcohol, are not numerous. They are, so far as I am aware:

[1] *Loc. cit.*
[2] J. Chem. Soc., 77, 1255 (1900).

$CuSO_4.4NH_3.H_2O$,[1]
$CuCl_2.4NH_3.H_2O$,[2]
$Cu(NO_3)_2.4NH_3$,[3]
$CuI_2O_6.4NH_3.3H_2O$,[3]
$CuS_2O_6.4NH_3$,[4]
$CuC_4H_4O_4.4NH_3$.[5]
$CuC_4H_4O_6.4NH_3$,[6]
$Cu(C_2H_3O_2)_2.2NH_3.2H_2O$,[5]
$Cu(SCN)_2.2NH_3$,[6]

and the oxalates:

$CuC_2O_4.NH_3$,
$CuC_2O_4.2NH_3$,
$CuC_2O_4.2NH_3.2H_2O$,
$CuC_2O_4.4NH_3.2H_2O$,
$CuC_2O_4.5NH_3$.

The number is scarcely large enough to warrant the assumption of any type as fundamental for *all* cuprammonium compounds.

If we add to these the salts that have been obtained by the action of dry ammonia on anhydrous copper salts, at ordinary temperatures, we find no added reason for assuming any fundamental type. These salts are:

$CuSO_4.5NH_3$,[7]
$CuCl_2.6NH_3$,[8]
$CuBr_2.6NH_3$.[9]

[1] Berzelius: *Loc. cit.*
[2] Kane: *Loc. cit.*
[3] Rammelsberg: Ann. d. Phys. u. Chem. (Poggendorff), 44, 569 (1838).
[4] Heeren: *Ibid.*, 7, 189 (1826).
[5] Schiff: *Loc. cit.*
[6] Meitzendorff: Ann. d. Phys. u. Chem. (Poggendorff), 56, 63 (1843).
[7] Rose, H.: *Ibid.*, 20, 150 (1830).
[8] Bouzat: Ann. Chim. Phys., [7], 29, 330 (1903. Rose and Bouzat: *Loc. cit.*
[9] Richards: Ber. d. chem. Ges., 23, 3790 (1890).

Rammelsberg[1] erroneously assigned to this last salt the formula $CuBr_2.5NH_3$.

There is no reason to believe that these latter salts are not as truly cuprammonium salts as are those in the preceding list. They simply happen to have been prepared in the absence of water, while the others have been prepared in its presence. Any generalization as to cuprammonium salts must include these compounds, or they must be shown to be a unique class of substances.

I regard it as more profitable, at present, to consider cuprammonium salts from the point of view of the equilibria that exist at the time the salts are forming. This conception has the advantage that it is sufficiently general to include, logically, the salts prepared from aqueous solutions and those prepared from anhydrous salts and dry ammonia, and in that it suggests experimental work that would, necessarily, extend the chemistry of cuprammonium salts. The facts that cupritetrammonium sulphate, chloride, nitrate and oxalate, when brought into the presence of water, at once undergo partial decomposition with the setting free of ammonia, and that, when solutions of copper sulphate, chloride, nitrate and oxalate are saturated with ammonia gas, the corresponding tetrammonium, or higher, salts are forced to crystallize gradually out of the solutions as the concentration of ammonia rises, suggest that cuprammonium complexes are formed only under definite conditions of relative concentrations of water, ammonia and copper salt. The three concentrations referred to are different for different complex salts of the same acid, and are different for the same complex salt of different acids. Thus, if we consider the dihydrated diammonium and tetrammonium oxalates, which are different complex salts of the same acid, obviously, from what has been said of their preparation, there is a higher relative concentration of ammonia and a lower relative concentration of water in the equilibrium equation for the tetrammonium salt than for the diammonium salt. If we consider two pentammonium salts, the same complex salt of different acids, it would seem that the

[1] Ann. d. Phys. u. Chem. (Poggendorff), **88**, 247 (1843).

relative concentration of water in the equilibrium equation for cupritetrammonium sulphate is much lower than the relative concentration of water in the equilibrium equation for the pentammonium oxalate, for the oxalate can be obtained from aqueous solutions, while the sulphate requires so low a relative concentration of water that this value has not yet been reached by introducing ammonia gas into an aqueous solution of copper sulphate; so that the pentammonium sulphate has, so far, only been produced under conditions where the relative concentration of water was almost nil, that is, when the anhydrous salt is treated with, approximately, dry ammonia.

It may be that the relative concentration of water is so low in the equilibrium equations for most cupripentammonium and higher cupriammonium salts that it cannot be attained by dissolving ammonia in the aqueous solution of the salt, or that it cannot readily be attained and, therefore, most of the pentammonium salts have not yet been prepared from aqueous solutions. The relative concentration of water is, in general, higher for tetrammonium salts than for pentammonium salts, and in many instances it can readily be attained in solutions, so that there are a number of well known tetrammonium salts that have been obtained from aqueous solutions. There are some instances where one would infer that this value for the relative concentration of water is so low that it is not easily attained by introducing ammonia into an aqueous solution of the copper salt, for in these cases the highest cuprammonium salts, so far obtained from aqueous solution, contain but 2 ammonia groups.

It follows that in systems where the relative concentration of water is very small or almost nil, at least as high cuprammonium salts should be obtained as in systems where the relative concentration of water is as low as it can be gotten by the introduction of ammonia gas into an aqueous solution of the copper salt. That is, the highest salt obtainable by treating the anhydrous salt with approximately dry ammonia must always contain at least as many ammonia groups as the highest salt of the same acid obtainable from aqueous solutions. It is to be expected that the highest salt obtainable by the treat-

ment of anhydrous salt with approximately dry ammonia will, in some cases if not in all, exceed in complexity the highest salt of the same acid obtainable from aqueous solution.

The number of salts that have been prepared from the anhydrous salts by the action of approximately dry ammonia is not large, but in every instance the salt thus obtained does exceed in complexity the highest salt of the same acid obtainable from aqueous solution by the introduction of ammonia gas.

This line of reasoning is consistent as long as there is no experimental fact against the assumption that, between the limits copper salt $+6NH_3$ and copper salt $+NH_3$, only the effects of mass action need be considered, and no such fact is known at present.

This method of consideration presupposes, throughout, that we are dealing with salts prepared at comparable temperatures, in systems containing nothing but copper salt, water and amnia.

Analytical Methods.

In general, the same methods have been used for determining copper and ammonia as have been described in a previous paper. Slight modifications, however, were adopted.

Because the oxalates could not be heated in the air without violent decomposition, the salts $CuC_2O_4.5NH_3$ and $CuC_2O_4.4NH_3.2H_2O$ were heated in hydrogen. The residues, consisting largely of metallic copper, were then heated in the air for half an hour with a view to completely oxidizing, by the copper oxide, any trace of organic matter that might remain after the decomposition in hydrogen. The copper oxide was then converted into cuprous sulphide, by Rose's method, and weighed. In the case of the salts $CuC_2O_4.2NH_3$ and $CuC_2O_4.NH_3$, it was impossible to get rid of the ammonia they contained by heating in the air or in hydrogen, for the decomposition invariably ended disastrously, from the point of view of quantitative analysis. Consequently these salts were treated with a little concentrated sulphuric acid and heated very cautiously until the evolution of gases ceased, the excess of sulphuric acid being subsequently volatilized at a higher tempera-

ture. The residues, consisting of anhydrous copper sulphate, were then converted to cuprous sulphide and weighed. The results for copper run almost uniformly low; I know of no other reason for this than that there may have been small and unavoidable losses of solid matter in both processes by which the salts were freed from ammonia.

The salts were weighed directly into an excess of concentrated hydrochloric acid when they were to be analyzed for ammonia. There was extremely rapid decomposition with loss of ammonia during the weighings of the salt $CuC_2O_4 \cdot 5NH_3$. Concentrated hydrochloric acid was used in the place of sulphuric acid, which had been used in the analysis of the cuprammonium sulphates, because the oxalates can be dissolved in hot, concentrated hydrochloric acid, whereas they are nearly insoluble in sulphuric acid. Better agreement among the results of parallel analyses was obtained when the oxalates had first been dissolved, before the addition of the alkali prior to distillation, than when they had not been dissolved.

CHEMICAL LABORATORY,
BRYN MAWR COLLEGE,
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REPORTS.

Preparation of Pure Ethyl Alcohol.

Commercial "absolute" alcohol always contains water, sometimes as much as 1–2 per cent; in addition to this, aldehyde is frequently present in varying quantity. The methods of purification in general use in laboratories, such as distillation over lime, baryta, sodium, etc., although adequate to remove the water, fail to affect the aldehyde and it cannot be eliminated by fractionation. The problem of its removal has been attacked recently by L. W. Winkler[1] in the following manner: Silver oxide, prepared from the nitrate, is well washed and dried at the ordinary temperature. It is then triturated with a little of the alcohol and the thin paste added to the remainder. The quantity of oxide used depends, of course, on the particular sample of alcohol; it need not exceed a few grams to the liter and may be less. To neutralize the acetic acid which is produced potassium hydroxide, 1–2 grams per liter, is added;

[1] Ber. d. chem. Ges., 38, 3612 (1905).

the mixture is frequently shaken and allowed to remain for several days at the ordinary temperature, until a portion of the alcohol fails to give the test for aldehyde with ammoniacal silver solution.

The author recommends metallic calcium, in the form of filings, for the removal of water from alcohol; 20 grams are usually sufficient to dehydrate 1 liter of commercial "absolute" alcohol. The substances are mixed and boiled in a distillation flask with a reversed condenser and then distilled; cork connections must not be used. The product is 99.9 per cent pure. A second treatment with 0.5 per cent of its weight of calcium appears to remove the last trace of water, because a third treatment, also with 0.5 per cent of calcium, was found to produce no further change. Certain physical properties of alcohol, purified in this manner and fractionally distilled, were determined with the following results: Sp. gr. at 0° = 0.80629, at 10° = 0.79787, at 15° = 0.79363, at 20° = 0.78937; these figures are reduced to a vacuum and referred to water at 4°. The corresponding values given by Mendeléeff are 0.80625, 0.79788, 0.79367 and 0.78945, respectively. The boiling points are 77°.81 (743.5 mm.), 78°.20 (754.9 mm.) and 78°.29 (757.8 mm.); therefore a difference of 1 mm. pressure causes a change of 0°.034 in the boiling point. The author mentions two rather curious facts which he has observed in the course of his work. The reaction between calcium and alcohol is the more vigorous the less water is present below 5 per cent, but ordinary alcohol, containing 5–10 per cent of water, also attacks calcium with considerable energy. Alcohol absolutely free from water is not nearly so hygroscopic as is usually supposed. For example, 200 cc. of it were allowed to remain in an uncovered beaker, exposed to the air of the laboratory, during 15 minutes; it was then found that the amount of water which had been absorbed was less than 0.1 per cent.

J. BISHOP TINGLE.

Stibine and the Allotropic Varieties of Arsenic and Antimony.

In some recent papers,[1] Stock and his assistants describe the methods of preparation and the general properties of several varieties of arsenic and antimony. As a preliminary to this work they made a very careful study of stibine,[2] which was obtained by the action of hydrochloric acid on an alloy of antimony and magnesium. Its physical constants and chemical and physiological action were worked out in detail. While 1 volume of water only dissolves 0.2 and an equal volume

[1] Ber. d. chem. Ges., 37, 4572; 38, 3837.
[2] *Ibid.*, 37, 885.

of alcohol dissolves 15 times its volume of the gas, carbon bisulphide dissolves, at 0°, not less than 250 times its volume of stibine. Its most characteristic chemical property is its great instability which, in some cases, produces a violent explosion without any apparent cause, especially during the evaporation of the liquefied gas. It is fairly stable for some hours, at ordinary temperatures, if it is dry and kept in clean vessels, but when the separation of the antimony once begins the speed of the decomposition rapidly increases. Moisture as well as oxygen and, more slowly, air cause a decomposition of the stibine, which is often complete in 24 hours. From a study of its physiological action it was concluded that some of the statements found in the literature regarding its toxicological effects are entirely erroneous. The pure gas when inhaled by mice produced instantaneous death, while exposure, for an hour, to air containing 0.01 its volume of the stibine, in most cases caused death after shorter or longer periods. Although the exact nature of its action is not known, it is, apparently, not due to any reaction with the blood.

The yellow modification of arsenic was first observed in 1867, but very little could be obtained owing to the ease with which it passes over into the black variety. Stock has devised a method by which it is possible to transform the black variety quantitatively into the yellow. A glass tube, sealed at one end, is filled to a height of 2 cm. with "kryptol", which can be heated by means of 2 insulated wires that pass to the top and bottom of the mass and end in two rings, the source of power being a storage battery. About the end of this tube is placed a small beaker containing some black arsenic. This part of the apparatus is introduced into a larger vessel, the joint being ground to make it air-tight. The whole apparatus is then placed in a double-walled vessel into which liquid air can be introduced to cool the inner vessel. If, now, the latter is exhausted and the kryptol is heated, the black arsenic is converted into a vapor and, by contact with the walls of the vessel, which are cooled by liquid air, is suddenly condensed as yellow arsenic. The kryptol is heated to 450° and the action is carried on in a room which is dark, or in one in which the substance is only exposed to red light, as sunlight or the ordinary artificial light changes the yellow variety into the black. The Welsbach light or an electric light causes this conversion slowly, even at the temperature of liquid air, while direct sunlight causes an instantaneous change if the vessel is not in the cooling agent. When the transformation was produced in the dark, by placing the tube containing the yellow arsenic in

a vessel of warm alcohol, there was no evidence of any light formed during the change, although a sharp cracking sound indicated the violence of the action. The authors proved the identity of this substance with that prepared by Erdmann and von Unruh, who obtained it by condensing arsenic vapors in carbon bisulphide and cooling the solution until the yellow arsenic separated out.

Antimony, like arsenic, exists in a yellow, a black and a metallic-gray variety. The yellow modification can be obtained by passing oxygen or air into liquid stibine at 90°, or by the action of chlorine on stibine at —100°, using liquid ethane as the cooling agent. The substance is only formed in small amounts, and is even more unstable than the yellow arsenic, as it becomes black in a few seconds at —50°. The black variety can be made by three methods: (*a*) by the transformation of the yellow variety; (*b*) by the action of oxygen or air on liquid stibine, at temperatures above —90°; and (*c*) by the rapid cooling of vapors of ordinary antimony. The variety obtained by these methods is different from the ordinary metallic variety. It has only been obtained in an amorphous condition, is more volatile and has a lower density than the gray, metallic variety. It is also more active chemically, as it is oxidized by air at the ordinary temperature. If the black variety is heated to 400° in a vacuum, it changes, instantaneously, to the gray variety, the appearance and density changing simultaneously, the same result being produced, slowly, by heating with water. The fact that the black variety is unstable even at ordinary temperatures explains why only the gray, metallic variety is found in nature. A substance which has been described by several investigators as black antimony is probably not a pure material.

The three elements, antimony, arsenic and phosphorus exhibit this interesting relation, that while, at ordinary temperatures, in the case of the first the metallic is the stable form, in the second it is the black, amorphous variety, and with the third, in the absence of light, the yellow form, and also the red, which are the more stable.

In this connection mention may be made of a recent article by Ruff and Graf,[1] in which they describe the method of preparation and properties of arsenic pentafluoride. This substance is quite easily obtained and is one of the most active fluorides. When antimony pentafluoride and arsenic trifluoride are brought together at the temperature of liquid air, a crystalline product separates. This is not the pentafluoride, but if bromine is added a heavy white vapor is formed, similar

[1] Ber. d. chem. Ges., 39, 67 (1906).

in appearance to that of sulphur trioxide in the air, and the mass becomes solid. The white vapor is due to the action of moisture on some of the vapors of the arsenic pentafluoride. The reaction can be expressed by the following equation:

$$2SbF_5 + AsF_3 + Br_2 = 2SbF_3Br + AsF_5.$$

If a glass apparatus is used all the connections must be sealed, as contact with organic materials, such as rubber, cork or grease, on stop-cocks will cause the formation of hydrofluoric acid. The apparatus must be most carefully dried to remove all traces of moisture. In order to separate the excess of bromine, the flask is removed from the vessel of liquid air and is allowed to stand until it reaches the temperature of the room, by which time all of the fluoride will have passed over into the receiver, which is cooled by liquid air, the bromine present in excess remaining in the first flask. The fluoride is a colorless gas, which liquefies at $-53°$ and solidifies at $-80°$. It is easily soluble in water and, when cold, does not attack dry glass. If, however, the glass is moist or the substance is heated, the glass is attacked with the formation of silicon fluoride and arsenic pentoxide. Silicon, when heated with the gas, forms silicon fluoride and arsenic. Sulphur, phosphorus, copper, zinc, iron and bismuth are all acted upon by the gas if heated slightly, while organic substances react very readily.

J. E. G.

REVIEWS.

RADIUM AND RADIO-ACTIVE SUBSTANCES. By CHARLES BASKERVILLE, PH.D., Professor of Chemistry and Director of the Laboratory, College of the City of New York, formerly of the University of North Carolina. Philadelphia: Williams, Brown & Earle. 1905. pp. 154. Price, $1.00.

In this volume the author has endeavored to present "a non-mathematical work on the subject of radium and its application in medicine," in a popular manner. For all details he refers the reader to the works of Rutherford, Soddy and others. The large number of observations recorded shows that the author has read the subject extensively and the references to the journals containing these would be of great service to the scientific investigator, but, unfortunately, they are honeycombed with errors. The English throughout is bad, even one well acquainted with the subject would have difficulty in interpreting the meaning of many sentences.

The book is divided into two parts, the first, consisting of 5

chapters, on the phenomenon and theories of radio-activity, and the second on the applications of radio-active substances in medicine. This latter portion is, as the author remarks, a collection of observations "impartially reported." In the first section many glaring mistakes occur, of which the following are a few: On p. 14, referring to the properties of β-rays, he says, "they do not discharge the electroscope, hence do not ionize gases," and p. 36, "the term, ray, is applied to a stream of corpuscles." It is considered by the leading physicists that the X-rays and, possibly, the so-called γ-rays are pulses in the ether. Then again, on p. 41, "the penetration of the α-emanations as found is;" and on p. 72 "the phenomenon" of the spinthariscope "is based upon the bombardment of the zinc sulphide screen by the emanations." Throughout the whole book the words ray and emanation are used more or less synonymously. It is surely unnecessary to say that the emanation from radio-active substances is well defined and is quite distinct from the rays.

Several references are made to the "elements" carolinium and berzelium; it is a pity that time did not permit the author to refer, even in a foot-note, to the work of Meyer and Gumperz,[1] published February, 1905, which, to say the least, renders the existence of these substances open to the gravest doubt.

The book, as a whole, is uninteresting, without the smallest spark of originality and cannot be of much use. The proof-reading was carelessly done, as mistakes in orthography and proper arrangement of the references abound. The printer, however, has done his work well, the type and paper are good and the illustrations satisfactory. JAMES BARNES.

SOILS AND FERTILIZERS. By HARRY SNYDER, B.S., Professor of Agricultural Chemistry, University of Minnesota, and Chemist of the Minnesota Experiment Station. Second edition. Easton, Pa.: The Chemical Publishing Co. 1905. Price, $1.50.

The first edition of this book appeared in 1899 under the title "The Chemistry of Soils and Fertilizers." In this edition the author has made so many additions and revisions as to materially change the scope of the work and necessitate the change of name. He states that the book, as now presented, includes all of the topics and laboratory practice relating to soils as outlined by the Committee on Methods of Teaching Agriculture, appointed by the Association of Agricultural Colleges and Experiment Stations.

In very clear and simple language Professor Snyder treats

[1] Ber. d. chem. Ges., 38, 817 (1905).

of the physical, geological and chemical properties of the soil, of nitrification, nitrogen of soil, air and farm manures, fixation, the different plant foods and fertilizers, domestic and commercial, the food requirements of crops and rotation and the preparation of soil for crops. The closing chapter contains directions for laboratory practice.

The book assumes that the student has some knowledge of elementary chemistry. It is an excellent manual. E. R.

RESEARCHES ON THE AFFINITIES OF THE ELEMENTS AND ON THE CAUSES OF THE CHEMICAL SIMILARITY OR DISSIMILARITY OF ELEMENTS AND COMPOUNDS. By GEOFFRY MARTIN, B.Sc. (LOND.). London: J. and A. Churchill. 1905. Price, $4.00.

This book is a study of the chemical affinities of the elements in their periodic relations.

The author's fundamental proposition is that the attractive, or chemical forces of an element determine its chemical properties, *i. e.*, its chemical reactions, its volatility, fusibility, solubility, cohesion, etc., almost exclusively, because the attractive forces of the elements are vastly greater than any other force they exert.

He has compiled tables of data to establish the relative affinities of each element for every other element. This task was only possible, he says, because of the investigations which have been carried on within the last few years on the nitrides, carbides, borides, silicides, etc., of the elements.

Given the data for the relative affinities, it would be possible to express them graphically by series of curves or by surfaces. The author chooses the latter method. He expresses the affinities of elements by lines vertical to a surface. The affinity of chlorine for aluminium, for example, is less than that for sodium, greater than that for sulphur, and the vertical lines expressing these affinities would have lengths relatively proportional to the strength of the affinities.

He takes the Mendeléeff table as a surface. Supposing it is desired to express the affinities of chlorine: Erect on the table vertical lines for each element, placed in the position of the elements on the table. The length of each vertical is proportional to the affinity for chlorine of the element which it represents. Connect the verticals in each "series" of elements by a line passing through their summits, and the verticals *i. e.*, the "groups," by similar lines. The graphical result for the affinities of chlorine for

H						
Li	Be	B	C	N	O	F
Na	Mg	Al	Si	P	S	Cl
Cu	Zn	Ga	Ge	As	Se	Br
Ag	Cd	In	Sn	Sb	Te	I
Au	Hg	Tl	Pb	Bi		

is a surface as shown in the diagram for chlorine.

The author now arranges these surface diagrams in the order of their elements in Mendeléeff's table. He says they

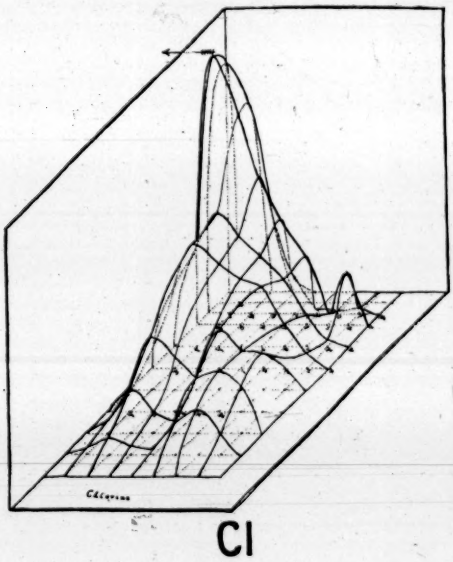

Fig. 1.

now "present the appearance of successive positions of an advancing wave whose crest, coming into the field of view on the extreme right hand of the diagram (of a given "series"), gradually sweeps from right to left, altering its form continually as it passes down the field, then passing out of view on

the left. This is followed by the appearance of a new crest on the extreme right (new "series") of nearly, but not quite the original form, ... each new crest heralding the appearance of a new cycle of elements. At the moment where the one crest passes out of view on the left and a second has not yet made its appearance on the right, we get an element of zero affinity, corresponding to the argon family.

It is difficult to make this quite clear without diagrams of a

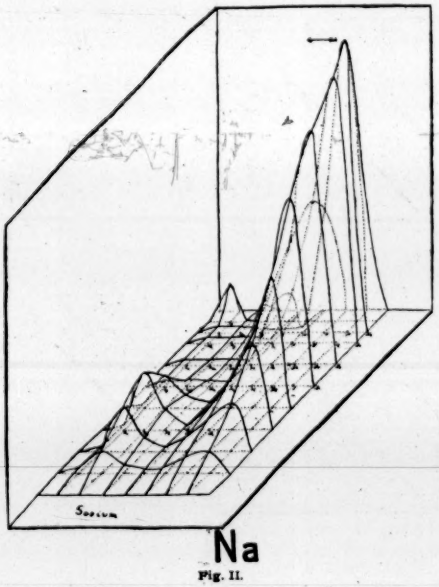

Fig. II.

complete series, which the space for a review will not permit. Diagrams are given of two elements, chlorine and sodium, which elements are at the two extremes of a wave, whose crest is on the left of the chlorine field; the wave assumes succes-

sive positions as it advances through the elements sulphur ➡ phosphorus ➡ silicon ➡ aluminium ➡ magnesium ➡ sodium, reaching in sodium a crest on the right of the field.

The periodicity of the affinities of elements thus shown, the author calls the "wave law," and he claims that it "explains" the periodic system. He believes that he is the first to discover and point out these relations.

The common wording of the periodic law is "The properties of an element are periodic functions of its atomic weight." Lothar Meyer and Mendeléeff included "attraction" or "affinity" among the properties of the elements, as every chemist knows, therefore, it seems to the reviewer, that the author's claim is unfounded.

The author seems to almost wilfully misunderstand things clear to others, from many examples one will suffice, he says: "It is a wide-spread notion that the molecular weight exercises a predominating effect in determining the melting and boiling points of compounds." Who ever claimed this, save in the case of homologous series of carbon compounds?

In brief, the author so ignores the work of others, puts forward such unwarranted pretensions to originality and, in parts of the book which need not be criticized here, indulges in such wild speculations that one would throw his book aside, were it not for the redeeming fact that he has done a very meritorious and extremely laborious piece of work in compiling the data and building up the diagrammatic surfaces. That the data are as complete as can be obtained at present, that the main conclusions he draws from his data are correct and that his graphic surfaces are an excellent expression of the periodic law, are facts sufficient to render his book noteworthy and valuable.

R. R.

NEUERE ANSCHAUUNGEN AUF DEM GEBIETE DER ANORGANISCHEN CHEMIE. Von PROF. DR. A. WERNER, in Zürich. Braunschweig: Druck und Verlag von Friedrich Vieweg und Sohn. 1905. pp. xii + 189. Price, unbound, M. 5; bound in linen, M. 5.80.

While the ordinary valence formulas answer very well for most carbon compounds, and even for most inorganic compounds, there are many compounds known, the constitution of which cannot be satisfactorily expressed by means of these formulas. This is not to say that the conception of valence is useless and has been superseded by a better conception. The phenomena of valence are just as real as they ever were, and it is just as important to study these phenomena to-day as it ever was. While we should very much like to know their cause, we may study them without touching the question as to their

cause. We have passed the stage in which it was held that the elements could be rigorously classified under a few heads as univalent, bivalent, trivalent, etc., and that, knowing the valence of the elements, the constitution of the compounds could be deduced. But still we come face to face with valence in every compound and cannot ignore it.

Many efforts have been made to enlarge and improve the conception of valence so as to fit it to certain complex compounds that in its ordinary form it is not competent to explain. Among these efforts that of Professor Werner has, perhaps, attracted most attention. He has shown that the metal-ammonia bases and the double salts can be explained by an interesting extension of the valence hypothesis. His views have been presented in a number of articles which have appeared during the past fifteen years and are well known to chemists. Further, many experimental investigations have been carried out with the object of testing certain conclusions to which Werner's hypothesis leads. This is not the place to discuss the hypothesis. It is sufficient to say that it is of value because it suggests questions that can be answered by experimental means and hence it has contributed and is contributing to the advance of chemistry.

In this book the author has presented his views systematically and clearly and has shown their applicability to the subject of constitution in general. In his preface he says: "It appears to be opportune to present in connected form the views which are to-day of importance for the structural and spatial conception of the molecules of inorganic compounds. We are, however, thoroughly aware that our new conceptions are pictures which, like every other scientific hypothesis, can only serve, as Mach expresses it, to economize thinking and describing. Should these pictures later be replaced by better ones nearer the truth, they will at least have served to pave the way towards a systematization of the almost innumerable facts of inorganic chemistry."

Every chemist ought to study this book. It will not be sufficient to read it. I. R.